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Spray liquid-liquid extraction columns :

Prediction of limiting holdup and flooding rates

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Abstract—The dispersed phase holdup for spray columns can be related to the phase flow rates by the following equation, derived originally for packed columns [5] and applied subse quently to pulsed [10] and rotary annular columns [11] :

$$\frac{V_d}{x} + \frac{V_c}{1-x} = \epsilon \bar{v}_0 (1-x)$$

In this expression, $\bar{v}_0$ is the characteristic velocity identified as the mean relative velocity of the droplets extrapolated to essentially zero flow rates.

Differentiation of the above equation, treating x as the independent variable, gives expressions which have been used to correlate flood point data in terms of $\bar{v}_0$ [10, 11]. It has also been shown that the limiting holdup at the flood point is dependent only on the phase flow ratio and is independent of the physical properties of the system.

In the case of spray columns, it has been found possible to predict $\bar{v}_0$ on the basis of the normal correlation of the free falling velocity for spheres, assuming the droplet size to be given by HAYWORTH and TREYBAL's relationship [6]. The entire flooding curve can thus be predicted for any system in terms of its physical properties and the dispersed phase nozzle geometry.

Résumé—Les auteurs ont montré que le hold up de la phase dispersée dans les colonnes à pulvérisation peut être relié à son débit par l'équation suivante, obtenue originellement pour des tours à garnissage et appliquée par la suite aux colonnes pulsées et à disques tournant :

$$\frac{V_d}{x} + \frac{V_c}{1-x} = \epsilon \bar{v}_0 (1-x)$$

Dans cette expression, v_0 est la vitesse caractéristique identifiée à la vitesse moyenne relative des gouttelettes extrapolées à des débits rigoureusement nuls.

La différentiation de l'équation ci-dessus, x étant considéré comme variable indépendante, donne des expressions utilisées à relier le point d'engorgement en fonction de $\bar{v}_0$. Ils ont aussi montré que le hold up limite au point d'engorgement ne dépend que du rapport des phases et est indépendent des propriétés physiques du système.

Dans le cas des colonnes à pulvérisation, les auteurs ont montré qu'il était possible de calculer $\bar{v}_0$, en se basant sur les vitesses normales de chute libre de sphères, avec l'hypothèse que la grosseur dex gouttes est donnée par la relation de HAYWORTH et TREYBAL. La courbe d'engorgement toute entière peut alors être calculée pour un système quelconque au moyen de ses propriétés physiques et de la forme géométrique de l'ajutage de dispersion.

1. INTRODUCTION

IN THE design of spray towers for liquid-liquid extraction operations, a knowledge of the limiting flow rates of the two phases is necessary before the column diameter can be calculated, and with this object in view a number of equations have been proposed for correlating flooding data in spray towers. Thus COLBURN [3] suggested plotting $V_d/\Delta\rho$ against V_c/V_d as abscissa on logarithmic co-ordinates, but this was not successful in bringing together the results obtained for different systems. Some improvement could be obtained by dividing the ordinate by the square root of the droplet diameter, but the correlation was not good.

A semi-theoretical equation, incorporating the droplet diameter and two empirical constants, was proposed by BLANDING and ELGIN [1], but as pointed out by these authors, their relationship was not an exact representation of the flooding mechanism and required some labour in its manipulation. ELGIN and FOUST [4], using solid spheres instead of deformable liquid droplets, obtained data which paralleled those of BLANDING and ELGIN, and a method of correlation was proposed which was based upon a knowledge of the particle diameter and upon the assumptions that the same factors are operative in spray towers and fluidized beds, and also that the void fraction – Reynolds number relation of WILHELM and KWAUK [13] is the same for the two. However, calculations of the holdup at the flooding point, based on the latter assumption, gave values in the neighbourhood of 0·05 [12], whereas experimental determinations are usually in the range 0·10-0·45 and can, in theory, range from 0-0·50, as will be shown later.

MINARD and JOHNSON [8], in an extensive study of spray column behaviour using a variety of aqueous-organic systems, obtained a semi-theoretical equation involving the droplet size and the dispersed phase holdup at flooding, based upon an extension of BERTETTI's theory for gas-liquid packed towers. In order to translate the equation into a more usuable form, the droplet size and the holdup were replaced by an experimentally determined "nozzle constant." However, the necessity of having to determine this constant for each particular nozzle geometry imposes an immediate limitation on the method. Another correlation involving droplet size and holdup at flooding has been proposed by SAKIADIS and JOHNSON [9] who, in an attempt to simplify their result, dropped the term $\left(1 + \frac{1}{2x}\right)^{0.75}$ on the grounds that this quantity tends to approach unity at high holdups. However as pointed out previously, the fact that x only tends to 0·50 in the limit renders this procedure questionable.

Of the methods available for the prediction of holdup at the flooding point, that proposed by WILHELM and KWAUK has been mentioned above, but was discounted on the grounds that it gave values which were on the low side. Both MINARD and JOHNSON and SAKIADIS and JOHNSON derived expressions for the holdup in terms of the limiting flow rates, the densities of the phases and the droplet size. However, the latter expression which is derived for true flooding conditions as opposed to total rejection indicates a fractional holdup of unity at zero continuous phase flow, which is contrary to experimental evidence [8], the limiting value being 0·50 as will be shown below. In this connection BLANDING and ELGIN reported that "in no case did the holdup tend to equal in volume that of the column, or to fill it. A tendency for the discontinuous phase to coalesce and become continuous, filling the column at flooding, was found only with end designs which produced marked coalescence at the entrance to the column." It will be seen therefore, that no entirely satisfactory method of estimating the limiting holdup has yet been proposed.

Since previous work had shown [1, 8] that spray columns could be operated up to the flooding point with little coalescence of the dispersed phase, it seemed reasonable to suppose that the data could be correlated by the same method as that used previously for pulsed and rotary annular columns [10, 11]. In the present paper, equations are presented which enable the limiting holdup to be calculated from a knowledge of the flow ratio only and, used in conjunction with HAYWORTH and TREYBAL's equation [6] for droplet size, can be used to predict the effect of variations in physical properties and nozzle diameter on the flooding rate.

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2. Theoretical Treatment

(a) *Limiting Flow and Holdup Equations*

It has been shown [5], that for packed columns, the dispersed phase holdup can be related to the phase flow rates by the equation :

$$\frac{V_d}{x} + \frac{V_c}{1-x} = \epsilon \overline{V}_0 (1-x) \qquad (1)$$

where $\overline{V}_0$ is the characteristic velocity, identified as the mean relative velocity of the droplets extrapolated to zero flow rates. Plots of this equation in the form V_d and V_c against x for a typical value of $\overline{V}_0 = 500$ ft/hr are shown in Fig. 1. Although equation (1) is cubic, only the root which lies between zero and the flooding point values of V_d and V_c is realizable in practice. These portions of the holdup curves are indicated by the full lines in Fig. 1.

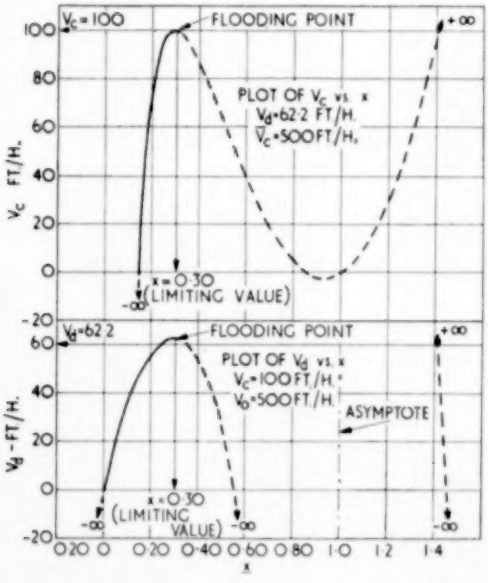

Fig. 1. Plot of Eq. (1) in the form V_d and V_c against x for a typical value of $\overline{V}_0 = 500$ ft/hr.

Equation (1) was found [10, 11] to be applicable up to the flooding point for mechanical columns, because in these cases coalescence is reduced to a minimum and the droplet size distribution for a given system is a function of the column geometry and the energy input only. Since it has now been shown [1, 8] that properly designed spray columns can be operated up to the flooding point with little or no coalescence of the dispersed phase, and that variations in droplet size over a wide range of nozzle velocities are not great [6], the holdup and flow rates are also related by equation (1). Consequently the droplet size and hence $\overline{V}_0$ will be substantially constant for a given column and system, and therefore $\overline{V}_0$ can be expressed as a function of the nozzle geometry and the physical properties of the system.

If the flow rate of one of the phases is fixed, an increase in the flow rate of the other phase will result in an increased value of the holdup until the flooding point is reached (see Fig. 1). It may be assumed that flooding occurs when V_d or V_c reach a maximum value, i.e., when dV_d/dx or $dV_c/dx = 0$. Since those portions of the holdup curves beyond the flooding point are unrealizable in practice, the value of x corresponding to the maximum flow rates also represents the limiting holdup at flooding, although this condition is not obtainable mathematically from equation (1).

Carrying out the differentiations described above :

$$V_d = 2\overline{V}_0 x_f^2 (1-x_f) \text{ when } (dV_c/dx) = 0 \qquad (2)$$

and

$$V_c = \overline{V}_0 (1-2x_f)(1-x_f)^2 \text{ when } (dV_d/dx) = 0 \qquad (3)$$

The value of x_f, the limiting holdup at the flooding point, is obtained by eliminating $\overline{V}_0$ between equations (2) and (3) and solving for x, thus :

$$x_f = \frac{(L^2+8L)^{0.5} - 3L}{4(1-L)} \text{ where } L = \frac{V_d}{V_c} \qquad (4)$$

A graphical solution of eq. (4) is given in Fig. 2.

It will be seen from eq. (4) that the limiting holdup can be expressed in terms of the flow ratio only, and is independent of $\overline{V}_0$. Furthermore, combining eqs. (2) and (3), and differentiating V_d with respect to V_c :

$$\frac{dV_d}{dV_c} = -\frac{x_f}{1-x_f} \qquad (5)$$

Consequently, the limiting holdup can also be evaluated directly from the slope of the flooding curve at any point. From the form of eq. (2) it

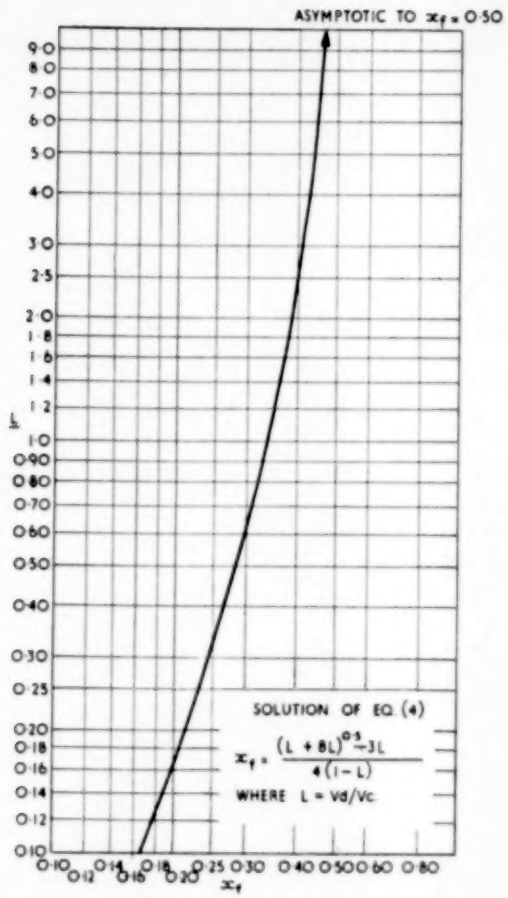

FIG. 2. Graphical solution of equation (4).

will be seen that a plot of V_d versus $x_f^2(1 - x_f)$ is a straight line through the origin of slope $2\overline{V}_0$. Such a plot is of use in correlating or extending incomplete flooding data, or conversely, if $\overline{V}_0$ is known for a particular system and nozzle configuration, it is possible to predict the entire flooding curve. Equations (2) and (3) can also be used to determine the limiting values of each flow rate as the other approaches zero. Thus when $V_d \to 0$, $x_f \to 0$ and $V_c = \overline{V}_0$ in the limit. Similarly, as $V_c \to 0$, $x_f \to 0.5$ and $V_d = \overline{V}_0/4$ in the limit. Furthermore, it will be apparent from eq. (5) that when V_d is plotted against V_c as abscissa, the curve meets the abscissa tangentially as $V_d \to 0$, but meets the ordinate with a slope of -1 as $V_c \to 0$. These conclusions are borne out experimentally and will be discussed further in Section 4 below.

(b) *Calculation of* $\overline{V}_0$

The droplet sizes produced by different diameter nozzles have been studied for a number of aqueous-organic solvent systems by HAYWORTH and TREYBAL [6], who obtained the equation :

$$\left.\begin{aligned} \frac{\pi d^3}{6} + 9.67 \times 10^{-10}\left(\frac{\rho_d \cdot v_N^2}{\Delta\rho}\right)\left(\frac{\pi d^3}{6}\right) \\ = 4.94 \times 10^{-9}\left(\frac{\gamma D_N}{\Delta\rho}\right) \\ + 4.91 \times 10^{-4}\left(\frac{D_N^{0.75} v_N^{0.37} \mu_c^{0.19}}{\Delta\rho}\right)^{3/2} \end{aligned}\right\} \quad (6)$$

which relates the droplet size to the nozzle diameter, physical properties of the system, and the velocity v_N of the dispersed phase through the nozzle.

Writing $\overline{V}_0$ in terms of the droplet diameter [2] :

$$\overline{V}_0 = 5.56 \times 10^{-4}\frac{d^2 \Delta\rho g}{\mu_c k}. \quad (7)$$

HAYWORTH and TREYBAL evaluated k over a wide range of variables and obtained the expression :

$$k = \frac{2.28 \times 10^3 D_N^{0.75}}{v_N^{0.64} \mu_c^{0.81}} \quad (8)$$

Substituting for k in eq. (7) and replacing d in terms of $\overline{V}_0$ in eq. (6), it is seen that

$$\left.\begin{aligned} 4.34 \times 10^9\left(\frac{\overline{V}_0^{3/2} \mu_c^{0.29} D_N^{1.13}}{\Delta\rho^{3/2} g^{3/2} v_N^{0.96}}\right) \\ + 2.58 \times 10^{-3}\left(\frac{\rho_d v_N^{1.36} \mu_c^{0.19} D_N^{0.75} \overline{V}_0}{\Delta\rho^2 g}\right) \\ = 4.94 \times 10^{-9}\left(\frac{\gamma D_N}{\Delta\rho}\right) \\ + 4.91 \times 10^{-4}\left(\frac{D_N^{0.75} v_N^{0.37} \mu_c^{0.19}}{\Delta\rho}\right)^{3/2} \end{aligned}\right\} \quad (9)$$

Remembering from eqs. (2) and (3) that, at the flooding point when $V_c = 0$, $V_d = \overline{V}_0/4$, then

$$\overline{V}_0 = \frac{4L_d}{A}, \quad (10)$$

and by definition

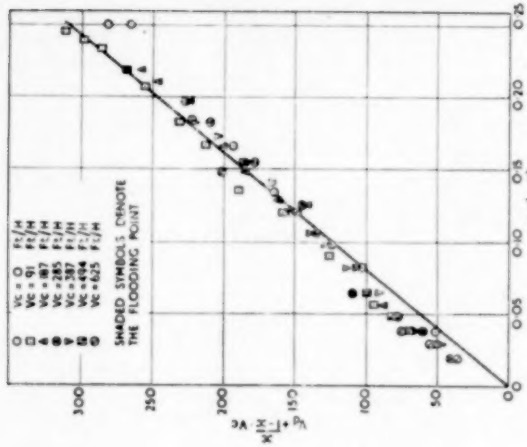

Fig. 3. Plot of holdup data for the system ethylene dichloride dispersed in water.

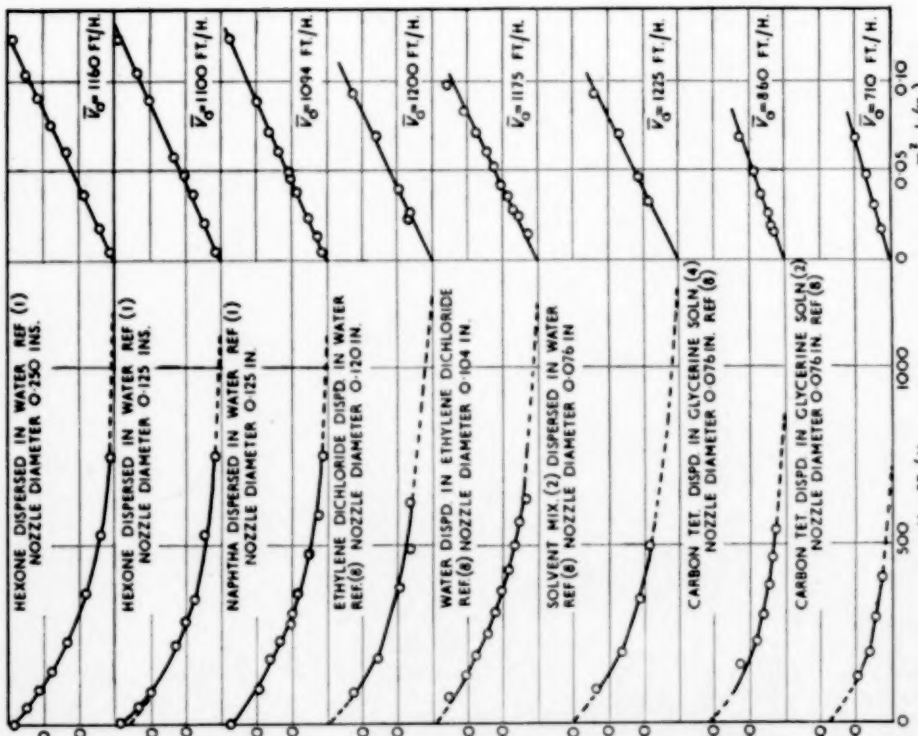
HEXONE DISPERSED IN WATER REF (1) NOZZLE DIAMETER 0·250 INS.
HEXONE DISPERSED IN WATER REF (1) NOZZLE DIAMETER 0·125 INS.
NAPHTHA DISPERSED IN WATER REF (1) NOZZLE DIAMETER 0·125 IN
ETHYLENE DICHLORIDE DISPD IN WATER REF(6) NOZZLE DIAMETER 0·120 IN.
WATER DISPD IN ETHYLENE DICHLORIDE REF (6) NOZZLE DIAMETER 0·104 IN
SOLVENT MIX (2) DISPERSED IN WATER REF (6) NOZZLE DIAMETER 0·076 IN
CARBON TET. DISPD IN GLYCERINE SOLN (4) NOZZLE DIAMETER 0·076 IN. REF (6)
CARBON TET. DISPD IN GLYCERINE SOLN (2) NOZZLE DIAMETER 0·076 IN REF (6)
$\bar{V}_0$ 1160 FT/H.
$\bar{V}_0$ 1100 FT/H.
$\bar{V}_0$ 1094 FT/H.
$\bar{V}_0$ 1200 FT/H.
$\bar{V}_0$ 1175 FT/H.
$\bar{V}_0$ 1225 FT/H.
$\bar{V}_0$ 860 FT/H.
$\bar{V}_0$ 710 FT/H.
V_c – FT/H
V_d – FT/H
x_f^2 1–(x_f)
(a)
(b)

Fig. 4. (a) Plots of typical flooding data extrapolated in accordance with Eqs. (2) and (3).

Fig. 4. (b) Linear plots of the same data.

$$v_N = \frac{L_d}{aN}. \qquad (11)$$

Combining eqs. (10) and (11),

$$v_N = \frac{A}{4aN} V_0$$

Finally, substituting for v_N in eq. (9), and re-arranging :

$$\left.\begin{aligned} & V^{0.55}\left[\frac{D_N^{1.13}\mu_c^{0.29}}{\Delta\rho^{1.5}}\right] \\ & \left[\frac{1.64\times10^{10}}{g^{1.5}}\left(\frac{aN}{A}\right)^{0.96} - 2.29\times10^{-4}\left(\frac{A}{aN}\right)^{0.56}\right] \\ & + V_0^{2.36}\left[3.91\times10^{-4}\,\frac{D_N^{0.75}\mu_c^{0.19}\rho_d}{\Delta\rho^2 g}\left(\frac{A}{aN}\right)^{1.36}\right] \\ & - 4.94\times10^{-9}\left(\frac{\gamma D_N}{\Delta\rho}\right) = 0. \end{aligned}\right\} \qquad (12)$$

Equation (12) enables V_0 to be determined for any particular system, column and nozzle geometry, and is readily solved by setting the equation equal to y and plotting this quantity against assumed values of V_0. The value of V_0 corresponding to $y = 0$ is then the solution of eq. (12).

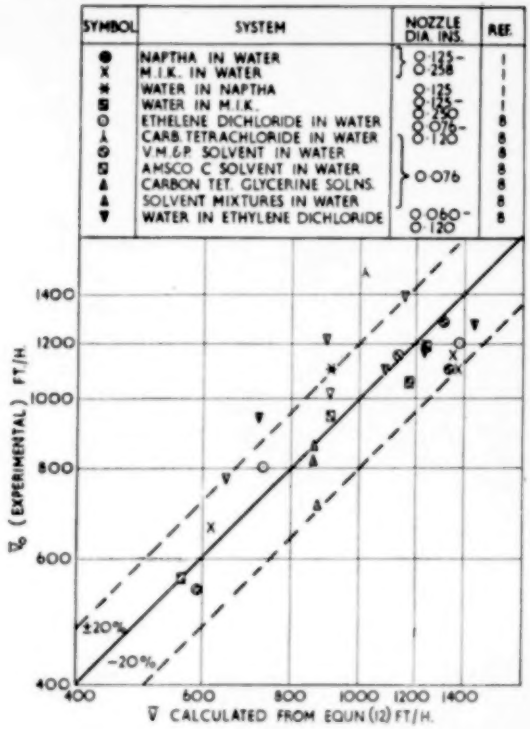

FIG. 5. Plot of experimental values of V_0 versus values calculated from eq. (12).

3. APPLICATION TO PUBLISHED DATA

The applicability of eq. (1) is demonstrated graphically in Fig. 3 for the system ethylene dichloride dispersed into water, for which the holdup values were determined by the pressure drop method [8].

Some typical flooding curves for a number of aqueous-organic solvent systems [1, 8] are shown in Fig. 4 (a); these are extrapolated to zero flow rates in accordance with eqs. (2) and (3). The corresponding linear plots of eq. (2) for the same data are shown in Fig. 4 (b), and in these cases, the values of x_f employed were calculated from a knowledge of the flow ratios using eq. (4). All the available flooding data [1, 8] were plotted in the manner shown in Fig. 4 (b), and the values of V_0 for the various systems were calculated from the slopes of the resultant plots. A graphical comparison between these V_0 values and those calculated from eq. (12) is shown in Fig. 5.

A graphical comparison between the limiting holdup values determined experimentally and those calculated from eq. (4) is shown in Fig. 6.

4. DISCUSSION

It will be seen from Fig. 3 that holdup data determined both below and at the flooding point can be related to the phase flow rates by eq. (1). There is some deviation from linearity below 8% holdup, the reported values being on the low side, but this may well be associated with the difficulty of making accurate measurements in this region. The slope of the plot gives a V_0 value of 1250 ft/hr as opposed to a value of 1380 ft/hr calculated from eq. (12). If the flooding data only are plotted in accordance with eq. (2), as shown in Fig. 4 (b), the value of V_0 derived from the slope of the plot is 1200 ft/hr which is in good agreement with the value obtained from Fig. 3.

The validity of eqs. (2), (3), (4) is well demonstrated in Figs. 4 (a) and 4 (b). In the first

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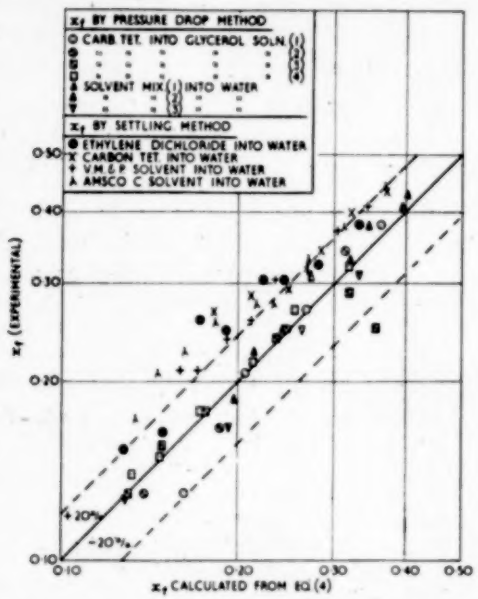

FIG. 6. Plot of experimental values of x_f versus values calculated from eq. (4).

diagram some typical flooding curves are shown for a number of systems, and it will be seen that these extrapolate well to zero flow rates of each phase. Thus, as shown previously, when $V_c = 0$, $V_d = \bar{V}_0/4$, and when $V_d = 0$, $V_c = \bar{V}_0$, where the appropriate value of $\bar{V}_0$ is obtained from the slope of the corresponding linear plot in Fig. 4 (b). A plot of the $\bar{V}_0$ values obtained in this way against those calculated from eq. (12) is shown in Fig. 5.

When determining values of $\bar{V}_0$ from a plot of eq. (2), points corresponding to a dispersed phase velocity through the distributer nozzles greater than 1 ft/sec were discarded, since velocities in excess of this figure give rise to droplet sizes which are erratic and non-reproducible [6]. It will be seen that the majority of the calculated values lie within $\pm$ 20% of the experimental values. Those values which lie outside this region tend to be on the high side, but this is to be expected, since MINARD and JOHNSON [8] defined flooding as the point at which the solvent phase was totally rejected from the column entry cone, rather than the true Elgin flooding point at which the solvent phase was just rejected from the column proper.

Fig. 6 shows a comparison between values of the limiting holdup calculated from eq. (4) and values obtained by the settling method, and from pressure drop measurements across the column. There is good agreement between the calculated values of x_f and those determined from pressure drop measurements, but in all cases the values determined by allowing the two phases to settle out in the column are consistently high. These latter values, shown in Fig. 6, are values reported by MINÅRD and JOHNSON, multiplied by the factor 0·92. This correction is necessary since, in the present case, we are considering the holdup in the column only, whilst the above workers defined their fractional holdup as the ratio of the height in the column occupied by the settled dispersed phase to the height of the interface above the dispersed phase nozzle [7]. It is probable that holdup values determined by the pressure drop method are inherently more accurate than those determined by settling since, in the latter case, the dynamic level of the dispersed phase in the disengaging section of the column was not amenable to accurate measurement. Consequently these values cannot be considered to have an accuracy greater than $\pm$ 10% [7].

In the cases of rotary annular and pulsed columns, the droplet size is a function only of the energy input, column geometry, and physical properties of the system, and is independent of the phase flow rates. In the present case, however, some dependence of droplet size upon the nozzle velocity of the dispersed phase has been demonstrated [6]. However, in general, the variation over a fairly wide range of nozzle velocities is not great, the droplet size tending to increase with velocity up to 10 cm/sec and then decrease with velocity up to 30 cm/sec. Thus, over a tenfold range of nozzle velocities from 2 to 20 cm/sec, HAYWORTH and TREYBAL [6] reported droplet sizes for the water/benzene-alkaterge system varying from 9·3 to 10·1 mm using a 7·86 mm nozzle, and from 4·8 to 5·9 mm using a 1·55 mm nozzle. Since the nozzle velocity influences the droplet size by virtue of its contribution to the

kinetic energy of the issuing droplet, it seems reasonable to suppose that the influence of the continuous-phase velocity will also be small.

With these considerations in mind, $\overline{V}_0$ was assumed to be substantially independent of phase flow rates in eq. (1), with the result that eqs. (2), (3), (4) are considerably simplified whilst representing the data adequately, as shown in Figs. 4 and 6.

It is of interest to note that although there is a tendency for the droplet size to decrease with nozzle velocities higher than 10 cm/sec, the dispersed phase holdup increases, thereby increasing the probability of droplet coalescence. It may well be therefore that, at high solvent flow rates, these two opposing effects should result in a substantially stable droplet size distribution.

5. CONCLUSIONS

(a) The dispersed phase holdup in a spray extraction column can be related to the superficial phase velocities and the characteristic droplet velocity by means of eq. (1).

(b) The holdup at flooding is independent of the droplet size, and can be predicted from a knowledge of the flow ratio alone by means of eq. (4).

(c) Flooding data can be extended and correlated in terms of the characteristic velocity by means of eqs. (2) and (4).

(d) The characteristic velocity for any given system and nozzle geometry can be calculated with an accuracy of $\pm 20\%$ from eq. (12).

Acknowledgements—Thanks are due to Mr. A. S. WHITE for his interest in this work. The help of Messrs. LOGSDAIL and WILLS is also gratefully acknowledged for assistance with the calculations.

NOTATION

A = cross-sectional area of column – ft².
a = cross-sectional area of dispersed phase nozzle – ft².
D = diameter of dispersed phase nozzle – ft.
g = acceleration due to gravity – ft/hr².
N = number of dispersed phase nozzles.
v = superficial phase velocity – ft/hr.
$\overline{V}_0$ = characteristic velocity of droplets – ft/hr.
x = fractional holdup of dispersed phase.
ρ = density – lb/ft³.
$\Delta\rho$ = density difference of phases – lb/ft³.
μ = viscosity – lb./ft.hr.
γ = interfacial tension of phases – lb/hr².
ϵ = fractional voidage of packing (unity for spray columns).

Subscripts

c = continuous phase
d = dispersed phase
f = at flooding

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On the characteristics of a non-isothermal chemical reactor†

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Abstract—The temperature reaction history in a chemical reactor is analysed. A practical method is outlined for obtaining particular solutions of the pertinent differential equation for specific values of the parameters which control the heat transfer and the reaction kinetics of the system. With help of a phase plane analysis, properties of the general solution of the differential equation are established which exhibit the influence of the above mentioned parameters on the temperature reaction history. The analysis indicates two physically distinct operational ranges of the reactor which depend essentially on the exterior heat transfer characteristics of the system.

Résumé—L'auteur étudie mathématiquement l'évolution de la température de réaction dans un réacteur tubulaire. Il ébauche une méthode pratique d'obtention des solutions particulières de l'équation différentielle appropriée pour des valeurs spécifiques des paramètres qui contrôlent l'échange thermique et la cinétique de la réaction du système. Par une analyse dans un plan, l'auteur établit les propriétés de la solution générale de l'équation différentielle qui prouvent l'influence des paramètres mentionnés ci-dessus sur la variation de la température de la réaction. L'analyse montre l'existence dans le réacteur de deux domaines opérationnels physiquement distincts qui sont fonction essentiellement des caractéristiques d'échange thermique avec l'extérieur du système.

INTRODUCTION

THE problem of determining the temperature history and the history of the reaction products in a flowing gas stream in which a chemical reaction occurs is of considerable importance in many fields of technology. It arises for example in the design of catalytic converters or homogeneous gas reactors in the chemical process industry. The interest in the thermal aspects of continuous flow reactors stems from the fact that many reactions must be held within relatively narrow temperature limits to be feasible. This requires provisions for heat exchange to prevent the occurrence of temperature excesses or deficiencies. The history of the reaction products, on the other hand, indicates the degree of completion to which the reaction has been carried out, and is thus an important parameter for an economic reactor design. The particular problem discussed below may be described as follows (see also [1]). An inert gas stream mixed with small quantities of reacting components capable of an exothermic reaction flows steadily through a long reactor tube of constant wall temperature. The entering gas stream which has been preheated to this temperature undergoes a chemical reaction as it passes through the tube. In its progress the mixed mean temperature of the gas rises at first with increasing distance from the entrance, since the amount of heat liberated by the chemical reaction exceeds the quantity of heat lost into the surrounding medium through the walls of the reactor. At a certain distance from the entrance the two effects attain an equilibrium and the gas temperature reaches a maximum. Thereafter, due to the consumption of reactive components, the mixed mean temperature of the gas decreases and attains the wall temperature on completion of the reaction.

The primary purpose of this paper is to determine the gas temperature as a function of the degree of completion of the reaction, the parameters which control the heat transfer, and the chemical reaction characteristics of the system.

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Although the above description and the analysis given below is applied to exothermic reactions, it can with minor modifications be extended to endothermic reactions as well. The problem outlined is not new. A number of analyses have been proposed which account for both the chemical kinetics and the transport properties in a flowing gas stream [2, 3, 4, 5].

In one model one assumes that the reacting gas possesses a uniform average velocity, concentration and temperature distribution transverse to its direction of flow. In this one-dimensional theory the heat transfer is assumed to occur entirely across a fictitious thermal boundary layer at the wall of the reactor. The process of heat transfer is described through the introduction of an empirical transport coefficient, the magnitude of which must be known a priori. In a more detailed description, which is usually based on a uniform velocity distribution, the temperature variation transverse to the direction of flow is taken into account. This avoids, then, the use of an overall heat transfer coefficient.

Either formulation of the problem leads to nonlinear differential equations of some complexity. Hence, nearly all solutions presented in the literature have been obtained by graphical or numerical methods for specific values of the parameters entering the problem. The results consequently lack the generality of an analytical solution. In this paper we shall be primarily interested in exhibiting both the qualitative and quantitative behaviour of the basic parameters, which characterize the heat transfer and reaction kinetics, on the average overall performance of the reactor. The model for the discussion will be the system described in terms of an empirical heat transfer coefficient. This will, of course, leave the finer details dealing with the transport properties out of discussion. These will be presented in a subsequent paper.

ANALYSIS

The following assumptions are made.

(1) Steady-state conditions exist in the reactor tube, which is of circular cross-section and constant wall temperature T_w along its entire length.

(2) The reactants form a slight admixture to an otherwise inert gas stream so that the molecular weight of the gas passing through the reactor remains essentially unchanged. The gas as a whole obeys the perfect gas law. All gas properties with exception of the density and temperature are assumed to be constant throughout the reactor.

(3) The velocity, temperature, density, and composition of the gas are assumed uniform at each cross-section of the tube, but vary in the direction of flow. The heat transport mechanism transverse to the direction of flow is taken into account in the form of Newton's law of cooling. Conduction and diffusion effects in the direction of motion are neglected.

(4) The temperature difference between the gas and the reactor wall is relatively small, i.e., $(T - T_w) \ll T_w$.

(5) The reaction is monomolecular and is assumed to follow the Arrhenius reaction rate law. Despite these restrictions the model described below exhibits the essential charactristics of a non-isothermal chemical reactor.

In view of the above assumptions, conservation of mass requires that

$$\rho u = G \text{ (a constant)} \tag{1}$$

where ρ is the density, u the velocity and G the mass velocity of the gas.

The kinetics of the reaction can be expressed in terms of ϵ $(0 \leqslant \epsilon \leqslant 1)$, the fractional completion of the reaction, by

$$\frac{d\epsilon}{dt} = u\frac{d\epsilon}{dx} = A(1 - \epsilon)\, e^{-E/RT}. \tag{2}$$

Here x is the distance from the entrance of the reactor, A the frequency factor, E the energy of activation of the reaction, R the gas constant (in thermal units) and T the temperature of the gas.

The expression for the conservation of energy for this model represents a balance between the heat carried by the gas stream, the heat liberated by the chemical reaction, and the heat lost through the wall of the reactor tube, i.e.

$$\rho u c\frac{dT}{dx} = Q\rho_r\, u\frac{d\epsilon}{dx} - \frac{4h}{D}(T - T_w). \tag{3}$$

Here Q represents the heat of reaction per unit

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mass of the reactant converted. ρ_r is the initial density of the reactant, h the overall heat transfer coefficient, D the diameter of the reactor tube and c the specific heat of the gas.

In addition one requires the equation of state

$$\rho = \left(\frac{PM}{R_0}\right)\frac{1}{T} \tag{4}$$

where M is the average molecular weight, P the gas pressure, and R_0 the universal gas constant. The associated initial conditions for equations (2) and (3) are

$$\epsilon(0) = 0\,; \quad T(0) = T_w. \tag{5}$$

The equations (1) to (5) define the model with which we shall be concerned. It is a mathematical model from which one can deduce the influence of the most important physical factors on the progress of the chemical reaction.

In view of assumption (4) the temperature rise in the gas stream is moderate enough so that one can write

$$\frac{1}{T} = \frac{1}{T_w}\left[\frac{1}{1+\dfrac{T-T_w}{T_w}}\right] \cong \frac{1}{T_w}\left[1 - \frac{T-T_w}{T_w}\right]. \tag{6}$$

The dimensonless excess temperature

$$\theta = \frac{T-T_w}{T_w}\frac{E}{RT_w} \tag{7}$$

having been introduced, the equations (2) to (4) become

$$u\frac{d\epsilon}{dx} = Ae^{-E/RT_w}(1-\epsilon)\,e^{\theta} \tag{8}$$

$$\rho uc\frac{RT_w^2}{E}\frac{d\theta}{dx} = Q\rho_r u\frac{d\epsilon}{dx} - \frac{4h}{D}\frac{RT_w^2}{E}\theta \tag{9}$$

$$\rho = \rho_w\left(1 - \frac{RT_w}{E}\theta\right) \text{ where } \rho_w = \frac{PM}{R_0T_w}. \tag{10}$$

The independent variable x can be eliminated between equations (8) and (9) with the result

$$\rho c\frac{RT_w^2}{E}\frac{d\theta}{d\epsilon} = Q\rho_r - \frac{4h}{D}\frac{RT_w^2}{E}\frac{1}{Ae^{-E/RT_w}}\frac{\theta\, e^{-\theta}}{1-\epsilon}. \tag{11}$$

On eliminating the density ρ with the help of (10) one obtains finally

$$\frac{d\theta}{d\epsilon} = \frac{1}{\left(1 - \dfrac{RT_w\,\theta}{E}\right)}\left\{\alpha - \beta\frac{\theta e^{-\theta}}{1-\epsilon}\right\} \tag{12}$$

where

$$\alpha = \left(\frac{Q}{cT_w}\frac{\rho_r}{\rho_w}\right)\left(\frac{E}{RT_w}\right) \text{and } \beta = \frac{4h}{Dc}\frac{1}{A\,\rho_w e^{-E/RT_w}}. \tag{13}$$

Equation (12), which is best suited for our purposes, will when integrated yield the dimensionless gas temperature θ as a function of the reaction history ϵ in terms of the essential parameters α, β and RT_w/E which describe the heat transfer and reaction characteristics of the system. The initial condition associated with equation (12) is, in view of (5),

$$\theta(0) = 0 \tag{14}$$

A general analytical solution of equation (12) in terms of elementary functions can unfortunately not be given. It is possible to obtain a series expansion in the parameters α, β and RT_w/E but little can be learned in this way about the essential nature of the solution. A more useful approach proceeds by a geometric phase plane discussion which, incidentally, yields also a practical method for solving equation (12) for any specific values of the parameters.

For the construction of a particular solution curve of equations (12) and (14) one can employ the isocline method. A lineal element field of equation (12) is constructed from

$$\frac{1}{\left(1 - \dfrac{RT_w\,\theta}{E}\right)}\left\{\alpha - \beta\frac{\theta e^{-\theta}}{1-\epsilon}\right\} = K \text{ (a constant)}. \tag{15}$$

Solving this for ϵ yields a family of curves, the isoclines

$$\epsilon = 1 - \frac{\beta/\alpha}{1 - \dfrac{K}{\alpha}\left(1 - \dfrac{RT_w\,\theta}{E}\right)}\theta e^{-\theta} \tag{16}$$

which are plotted in a θ, ϵ plane for a specific value of β/α, RT_w/E, α, and for different values of the parameter K. An isocline for a specific value of the parameter K is the loci of lineal elements of constant slope K, and the solution curve must cross this isocline with this slope.

Such a field is shown in Fig. 1 for the following

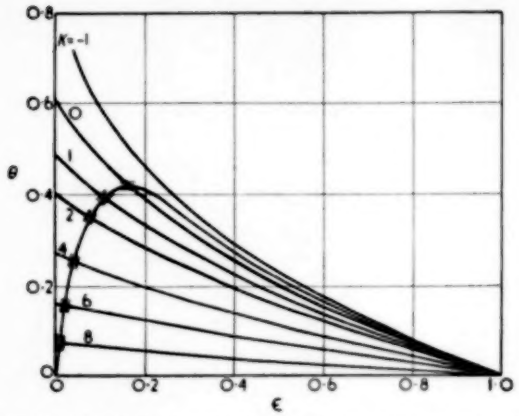

FIG. 1. The isocline field and particular solution curve of equation (12) for $\beta/\alpha = 3$, $\alpha = 10$, $RT_w/E = 1/10$.

values of the parameters: $\beta/\alpha = 3$, $\alpha = 10$, $RT_w/E = 1/10$. The solution curve, starting from the initial point (0·0) with a slope of 10 according to equation (12), rapidly attains a maximum, and falls subsequently to end in the point (0·1) as required by the completion of the reaction. By this graphical solution method any particular solution curve can be readily constructed and the temperature reaction history be determined. The construction of the isoclinal field becomes particularly simple if the term $RT_w\theta/E$ can be neglected with respect to unity, since in this case the members of the family (16) differ merely by a scale factor.

Having exhibited this convenient method for determining particular solutions for specific values of the parameters, we turn next to a detailed discussion of the properties of the general solution. Consider for this reason the complete isoclinal field of the differential equation (12) as shown in Fig. 2 for some particular values of the parameters α, β/α and RT_w/E. Within the circular sectors the isoclines are the loci of lineal elements of either positive or negative slope K, as indicated. Starting from the top and to the left of the line $\epsilon = 1$ and moving in a counterclockwise direction, the value of K increases from minus infinity to zero, changes sign and then increases from zero to plus infinity at the bottom of the line $\epsilon = 1$. A similar behaviour is encountered to the right of $\epsilon = 1$. All isoclines intersect at the point (0·1),

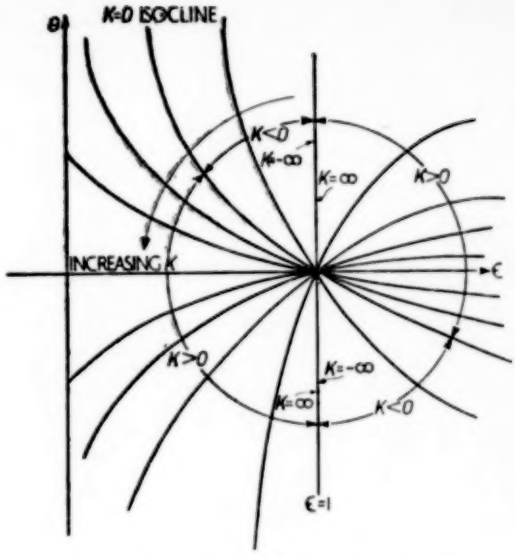

FIG. 2. The phase plane of equation (12).

which is a singular point of the differential equation (12).

The first question which comes to mind concerns the structure of any particular solution curve originating from the ordinary point (0·0) with slope α in accordance with equations (12) and (14). Will the solution curve terminate in the required point (0·1) or is it possible for it to miss this point? In the latter case only three distinct possibilities can arise as shown by curves *A*, *B*, and *C* in Fig. 3. In case *A* assume that the solution curve meets the ϵ axis somewhere between zero and one. In order to do this it must cross the $K = 0$ isocline, and hence would have a minimum or an inflection point with zero tangent at the crossing point. In the first case the curve would turn up, which is clearly impossible since the slope of the lineal elements above the isocline is negative. In the second case the solution curve would continue with a negative slope into a region where the lineal elements are positive. This rules out case *A*.

In case *B*, assume that the solution curve does not intersect the required point (0·1) because the curve turns upward and becomes asymptotic to the line $\epsilon = \epsilon_0$, $(0 < \epsilon_0 \leqslant 1)$. This is clearly impossible, since the slope of the solution curve

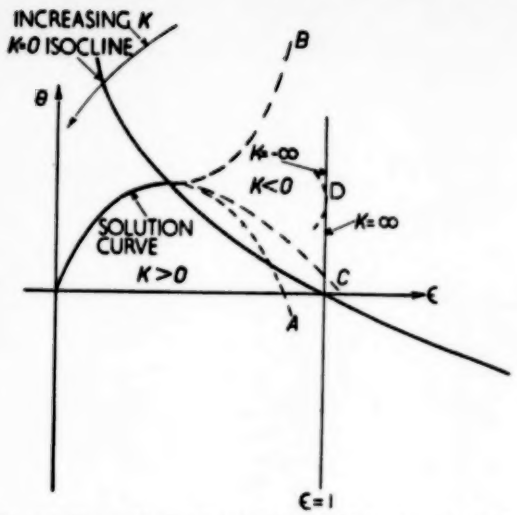

FIG. 3. Properties of the solution field in the neighbourhood of the singular point.

would be positive in a region where it must be negative. The third possibility is that the solution curve C assertedly intersects the line $\epsilon = 1$ at a point above the singular point. However, this is impossible, since the solution curve on approaching the line $\epsilon = 1$ from the left takes on an infinite negative slope, and hence cannot cross in any continuous fashion to the other side where the slope is positive and infinite. Consequently, the solution curve on approaching $\epsilon = 1$ will turn downward with infinite slope. Furthermore it cannot turn away, as shown by the segment D. Hence it must lead into the singular point. However, the solution curve with infinite negative tangent is not the only possibility of reaching (0·1) as we shall see by investigating the specific nature of the singularity. One concludes from the above that, for all finite values of the parameters, equation (12) has a solution which, starting from the point (0·0), must end in the singular point (0·1)

To gain further insight into the properties of the solution curves in the neighbourhood of the singular point, consider the appropriate form equation (12) takes close to this point. One can show in general [6] that the differential equation

$$\frac{dy}{dx} = \frac{ax + by + P(x, y)}{cx + dy + Q(x, y)} \tag{17}$$

in which the constants a, b, c, d are such that $ad - bc \neq 0$, and in which P and Q vanish as $x^2 + y^2$ does when $x, y \to 0$, has as its only singularities at the origin ($x = y = 0$) those of the much simpler equation

$$\frac{dy}{dx} = \frac{ax + by}{cx + dy}. \tag{18}$$

Equation (12) can be brought into this form by expanding the exponential term about $\theta = 0$ and neglecting all terms higher than the constant term. In addition, the co-ordinate origin is shifted to (0·1) by introducing the new variable $(1 - \epsilon)$. Hence

$$\frac{d\theta}{d(1-\epsilon)} = \frac{\beta\theta - \alpha(1-\epsilon)}{(1-\epsilon)}. \tag{19}$$

Without going into the details of the analysis here, it can be shown that the point (0·0) of equation (19) is a nodal point which has the characteristic that all solution curves passing through the immediate neighbourhood of this point will end in the singular point, as already found above. The shape of the solution curves near the singular point, aside from the trivial characteristic $\epsilon = 1$, is readily established by integrating equation (19), with the result

$$\theta(\epsilon) = C(1-\epsilon)^{\beta} + \frac{\alpha}{\beta - 1}(1-\epsilon), \beta \neq 1 \tag{20}$$

$$\theta(\epsilon) = C(1-\epsilon) - \alpha(1-\epsilon)\ln(1-\epsilon), \beta = 1.$$

From equation (20) one observes that for $\beta > 1$ the solution curve $\theta(\epsilon)$ becomes tangent to the straight lines of slope $\left(\frac{-\alpha}{\beta - 1}\right)$ as $\epsilon \to 1$. On the other hand if $\beta \leqslant 1$, the equations reveal that the slope of the solution curve ending in the singular point becomes negative and infinite. These properties allow one to define two distinct operational ranges of the reactor in terms of the parameter β.

Equation (13) shows that

$$\beta = \frac{\dfrac{4h}{c\,\rho_w\,D}}{Ae^{-E/RT_w}} = \frac{\dfrac{1}{\tau_{\text{conv}}}}{\dfrac{1}{\tau_{\text{chem}}}} \tag{21}$$

is the quotient of two reciprocal times. τ_{conv} is a characteristic relaxation time for the cooling of the reactor bed due to the overall heat transfer mechanism through the walls of the reactor, while τ_{chem} is a measure of the speed of the chemical reaction. A small value of β implies a small value for τ_{chem} and a large value of τ_{conv} or, in other words, a fast chemical reaction and a slow heat transfer exchange with the outside. As shown above, for values of $\beta \leqslant 1$, the solution curve ends in the singular point with infinite negative slope. This implies that the temperature of the gas falls primarily as a result of the final consumption of the reacting material as $\epsilon \to 1$, and not so much as a result of the overall heat loss. It seems appropriate to designate the operational range $0 < \beta \leqslant 1$, where the temperature maximum occurs close to $\epsilon = 1$, as the range in which the reactor behaves almost adiabatically. In this regime the temperature history is primarily determined by the progress of the chemical reaction and to a lesser extent by the overall heat transfer characteristics of the system.

On the other hand the solution curves for the operational range $1 < \beta < \infty$ enter the singular point with slope $\left(\frac{-\alpha}{\beta - 1}\right)$, which can result in solution curves of varying degrees of steepness with the temperature maximum occurring anywhere in the range $0 < \epsilon < 1$. This indicates that for this regime the exterior heat transfer plays an important role and is apparently the normal operating range for most industrial reactors.

The two cases are exhibited in a phase plane diagram in Fig. 4. Here the $K = 0$ isoclines of equation (12) are shown schematically for

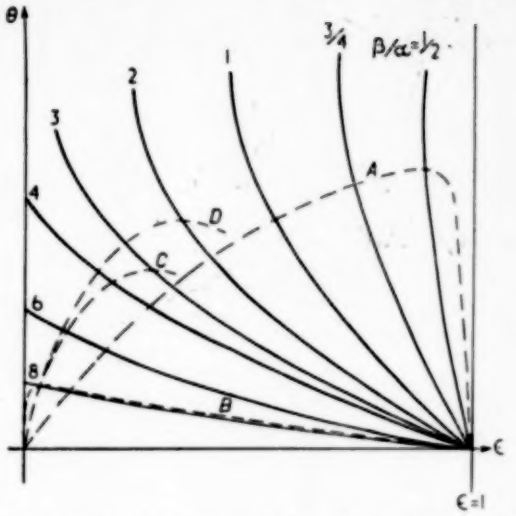

FIG. 4. The $K = 0$ isoclines for different values of β/α.

different ratios of β/α. Consider, for example, the operating condition $\beta = \frac{1}{2}$, $\alpha = 1$, $RT_W/E = 1/10$. The solution curve labelled A leaves the origin with slope 1, crosses the isocline $\beta/\alpha = \frac{1}{2}$ close to $\epsilon = 1$ with zero slope, and descends steeply to the singular point as shown. In contrast to this almost adiabatic behaviour, consider the reactor in the normal operating range $\beta = 120$, $\alpha = 15$, $RT_w/E = 1/10$ shown by curve B. The increased heat transfer decreases the temperature maximum considerably, and shifts the latter to a much smaller value of ϵ than in case A.

From Fig. 4 one can furthermore deduce the qualitative dependence of the solution on the parameters α and $\frac{\beta}{\alpha}$. Equation (13) shows that these parameters are a measure of

$$\left(\frac{\beta}{\alpha}\right) = \frac{4\,\dfrac{h}{D}\,\dfrac{RT_w^2}{E}}{Ae^{-E/RT_w}\,\rho_r Q} \approx \frac{\text{Heat loss per unit volume to the outside}}{\text{Heat generation per unit volume by the chemical reaction}} \tag{22}$$

while

$$\alpha = \frac{\dfrac{Q\,\rho_r}{c\,\rho_w}}{\dfrac{RT_w^2}{E}} = \frac{\text{Adiabatic temperature rise in the gas}}{\text{Effective temperature rise in the gas}}. \tag{23}$$

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Consider a fixed α and two different values of (β/α). The two solution curves labelled C and D are shown in Fig. 4. In agreement with physical expectation the solution with a smaller value of (β/α) attains a larger temperature maximum. One verifies, on the other hand, for a fixed value of (β/α) and two different values of α, that the solution curve with the larger α will have the larger temperature maximum. If one considers the maximum value of θ as a function of α and β/α, i.e., $\theta_{max} = \theta\,(\alpha, \beta/\alpha)$, one has $\left(\frac{\partial\theta_{max}}{\partial\alpha}\right)_{\frac{\beta}{\alpha}} < 0$ and $\left(\frac{\partial\theta_{max}}{\partial\frac{\beta}{\alpha}}\right)_{\alpha} < 0$, the subscript indicating the parameter which is held constant. The main conclusion in this case is that the temperature maximum in the reactor can be decreased with decreasing α and increasing β/α. One can substantiate this in the following limiting case which yields the temperature maximum as a function of the parameters. It is seen from Fig. 4 that for the complete range of α the maximum temperature is essentially controlled by the $K = 0$ isocline which depends only on the value of β/α. If the isocline for $K = 0$ intersects the line $\epsilon = 0$ at, say θ_0, then clearly $\theta_{max} < \theta_0$ for all α. One can improve this estimate by the following considerations.

For a sufficiently large value of β/α the maximum reactor temperature will be small enough for one to neglect the term $RT_W\,\theta/E$ with respect to unity in equation (12). Physically this amounts to the assumption that the density and velocity variations through the reactor are negligible. Equation (12) can then be written

$$\frac{1}{\left(\frac{\beta}{\alpha}\right)}\frac{d\theta}{d\epsilon} = \alpha\left(\frac{\alpha}{\beta} - \frac{\theta e^{-\theta}}{1-\epsilon}\right). \tag{24}$$

However, for this asymptotic condition one may neglect the derivative term on the left hand side almost everywhere except in the neighbourhood of the origin. Hence, for the greater part of the reaction history the θ, ϵ relation is given by

$$\epsilon = 1 - \frac{\beta}{\alpha}\theta e^{-\theta} \cong 1 - \frac{\beta}{\alpha}\theta \tag{25}$$

since θ is everywhere small. This is essentially the equation of the $K = 0$ isocline, which the solution curve follows closely. In the neighbourhood of the origin the solution of equation (24) will have the form

$$\theta = \alpha\epsilon + 0\,(\epsilon^2). \tag{26}$$

The value of θ at the intersection of the two curves approximates θ_{max} and is given by

$$\theta_{max} \cong \frac{1}{\frac{\beta}{\alpha} + \frac{1}{\alpha}}, \frac{\beta}{\alpha} > 1. \tag{27}$$

This asymptotic relation verifies the dependence of the two parameters on θ_{max} as discussed above.

Notation

A = frequency factor of monomolecular reaction, 1/h.
c = specific heat of gas, BTU/lb. °R.
D = reactor tube diameter, ft.
E = energy of activation, BTU/mol.
G = mass velocity of gas, lb./sq. ft. h.
h = heat transfer coefficient, BTU/sq. ft. h. °R.
K = slope values of lineal elements, defined by equation (15), dimensionless.
M = average molecular weight of gas, lb./mol.
P = gas pressure, lb./sq. ft.
Q = heat of reaction per unit mass of reactant converted, BTU/lb.
R = gas constant, BTU/mol. °R.
R_0 = universal gas constant, ft. lb./mol. °R.
T = gas temperature, °R.
T_w = reactor wall temperature, °R.
t = time, h.
u = gas velocity, ft./h.
x = distance from entrance of reactor, ft.
α, β = parameters defined by equations (13) or (22) and (23), dimensionless.
ϵ = degree of completion of the reaction, dimensionless.
θ = excess gas temperature defined by equation (7), θ_{max} its maximum value in the reactor, dimensionless.
ρ = density of gas, ρ_w its value based on reactor tube temperature, lb./cu. ft.
ρ_r = initial density of reactant, lb./cu. ft.

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On the condensation of a vapour of a binary mixture in a vertical tube

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Abstract—General differential equations for the condensation of a binary mixture in a cylindrical condenser are given. The solution for a specific case, viz in which the main body of the vapour is in turbulent flow, is presented. For simplified experimental conditions an equation presenting the temperature difference between the main vapour stream and the wall, as a function e.g. of the amount of condensate and of the partial coefficient of mass transfer in the vapour phase, has been derived.

Experiments on vapour mixtures of benzene and toluene, in a vertical condenser cooled with a liquid, have confirmed that the theoretical approach given can in some cases be used for the calculation of the condensation of a binary mixture. It also appeared that the partial coefficient of mass transfer in the vapour phase, which could be calculated with the aid of the equation derived, above a Reynolds number of 2,000, was a linear function of $Re^{0.8}$.

Résumé—On donne les équations différentielles générales pour la condensation d'un mélange binaire dans un condenseur cylindrique. On trouve la solution pour un cas spécial, à savoir le cas où la masse principale de vapeur est mise en courant tourbillonnant. Pour des circonstances expérimentales simplifiées, on a dérivé une équation dans laquelle la différence de température entre le courant principal de vapeur et la paroi est représentée comme une fonction p.e. de la quantité du condensat et du coefficient partiel du transfert de la masse dans la phase de vapeur.

Des expériences effectuées sur des mélanges de vapeur benzène-toluène dans un condenseur vertical, refroidi par liquide, ont confirmé que l'approximation théorique donnée peut, dans quelques cas, être employée pour calculer la condensation d'un mélange binaire. On a trouvé également que le coefficient partiel du transfert de la masse dans la phase de vapeur qui a pu être calculé à l'aide de l'équation dérivée, était, au-desus du nombre Reynolds de 2,000, une fonction linéaire de $Re^{0.8}$.

THE knowledge on the condensation of vapours of binary mixtures is of importance not only in itself but also for every non-adiabatic distillation of such mixtures. Only a few articles on this subject have appeared [1, 2, 3, 4]. From these the approach of COLBURN and DREW [4] to the present authors seemed interesting and will be included in the considerations put forward in the following.

THEORETICAL CONSIDERATIONS

One Component

For the film type condensation of a vapour consisting of a single component with the liquid film in laminar flow, the well-known NUSSELT [5] equation, existing in several forms, can be used. For the condensation in a vertical tube of a diameter, large compared with the thickness of the liquid film, the following differential equation can be derived (see Fig. 1):

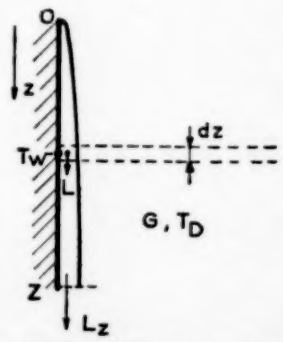

FIG. 1. Condensation of an unair system.

$$q = (\Delta H)_{T_D} \frac{dL}{S\,dz} = \frac{\lambda}{\delta_L}(T_D - T_W). \qquad (1)$$

After substituting: $\delta_L = \left(\frac{3\,\eta\,\Gamma}{\rho\,g}\right)^{1/3}$ in which $\Gamma = \frac{ML}{\rho S}$,

one obtains:

$$(T_D - T_W)\,dz = \left(\frac{3\,\eta\,M}{\rho^2 g S}\right)^{1/3} \frac{(\Delta H)_{T_D}}{S\,\lambda} L^{1/3}\,dL. \qquad (2)$$

Introducing a mean temperature difference between the vapour and the wall: $\overline{\Delta T} = (T_D - T_W)_m$ defined by:

$$\overline{\Delta T} = \frac{1}{Z}\int_0^Z (T_D - T_W)\,dz$$

and taking for η, ρ and λ constant mean values at the average film temperature, integration of (2) between $z = Z$ and $L = L_Z$ and $z = 0$ and $L = 0$ yields:

$$\overline{\Delta T} = 1{\cdot}082\left(\frac{1}{Z}\right)\cdot \frac{(\Delta H)_{T_D}}{\lambda}\cdot\frac{1}{S^{4/3}}\cdot\left(\frac{\eta M}{\rho^2 g}\right)^{1/3}\cdot L_Z^{4/3} \qquad (3)$$

or:

$$\overline{\Delta T} = A\,.\,L_Z^{4/3}$$

Two Components

Consider a vapour of a binary mixture which is partly condensed by flowing this mixture through a cooled vertical tube. The following assumptions will be made: (1) film condensation occurs; (2) the liquid is completely miscible; (3) the liquid is in laminar flow; (4) at the interface liquid-vapour the deviation from equilibrium is neglible; (5) the total molal concentration in each phase is constant; (6) the molal specific heat C_p is constant;)7) stationary conditions occur.

Two cases, viz. the vapour in laminar and turbulent flow, will be considered.

Vapour in laminar flow

Considering the vapour-phase and assuming that the molal flux (number of moles passing through the unit of area per unit of time) in the vertical direction (co-ordinate z) is p and in the radial direction (co-ordinate r) is n, the following differential equations can be derived:

From the total material balance

$$\frac{\partial p}{\partial z} + \frac{\partial n}{\partial r} + \frac{n}{r} = 0. \qquad (5)$$

From the material balance for the more volatile component A,

$$-D.C.\left(\frac{1}{r}\frac{\partial y}{\partial r} + \frac{\partial^2 y}{\partial r^2} + \frac{\partial^2 y}{\partial z^2}\right) + \left(n\frac{\partial y}{\partial r} + p\frac{\partial y}{\partial z}\right) = 0. \qquad (6)$$

From the heat balance

$$-\lambda\left(\frac{1}{r}\frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2} + \frac{\partial^2 T}{\partial z^2}\right) + C_p\left(n\frac{\partial T}{\partial r} + p\frac{\partial T}{\partial z}\right) = 0\,. \qquad (7)$$

A solution for these equations has not yet been found. It may be noted that the equations (6) and (7) are identical if the ratio $\frac{\lambda}{C_p D C} = 1$; that is, if the Lewis number $\frac{\lambda}{c_p \rho D} = 1$, because $C_p\,.\,C = c_p\,.\,\rho$.

Vapour in turbulent flow

If the greatest part of the vapour is in turbulent flow, and if it is assumed that in this region no horizontal temperature or concentration gradients exist, the equations derived can be applied to the small layer flowing in viscous flow around the turbulent kernel. (See Fig. 2).

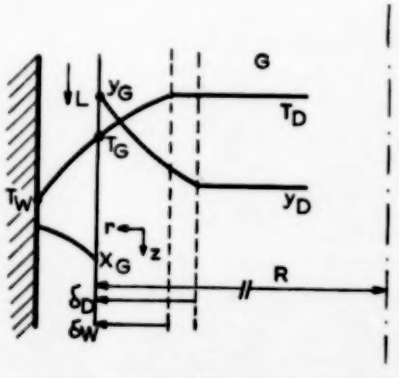

FIG. 2. Condensation of a binair system with the main body of the vapour in turbulent flow.

The thickness of this layer related to the diffusion is δ_D, related to the heat transport δ_W. It may be remarked that $\delta_W/\delta_D = (Le)^{1/3}$. Thus for $Le = 1$, $\delta_W = \delta_D$.

When this thickness is small compared with R, and assuming that p is constant in vertical direction, equation (5) yields: $\frac{\partial n}{\partial r} = 0$, and thus n is constant ($= N$) in radial direction. Moreover, for the thin layer, the temperature and concentration gradients in vertical direction can be neglected, compared with those in radial direction. Therefore the equations (6) and (7) can be simplified to

$$-D \,.\, C \,.\, \frac{d^2y}{dr^2} + N \frac{dy}{dr} = 0 \qquad (8)$$

$$-\lambda \frac{d^2T}{dr^2} + N \,.\, C_p \frac{dT}{dr} = 0. \qquad (9)$$

When the diffusion in the liquid film is negligible, the composition of the formed condensate is the same as the composition of the liquid at the the interface, x_G. Observing that (if r is taken from the "boundary" of the turbulent kernel) for $r = 0$, $y = y_D$, and for $r = \delta_D$, $y = y_G$, we can derive from equation (8):

$$\frac{x_G - y_G}{x_G - y_D} = e^{\frac{N}{DC}\delta_D}. \qquad (10)$$

From equation (9) it follows, because for $r = 0$' $T = T_D$, and for $r = \delta_W$, $T = T_G$, that

$$\frac{T - T_D}{T_G - T_D} = \frac{e^{\frac{NCp}{\lambda} z} - 1}{e^{\frac{NCp}{\lambda}\delta_W} - 1}. \qquad (11)$$

The heat flux to the liquid film by conduction (q_λ) is

$$q_\lambda = -\lambda \left(\frac{dT}{dr}\right)_{r=\delta_W} =$$

$$= (T_D - T_G) \frac{N \cdot Cp}{1 - e^{\frac{-N \cdot Cp \cdot \delta_W}{\lambda}}}, \qquad (12)$$

and by condensation (q_c) is

$$q_c = N\,(\Delta H)_{T_G}. \qquad (13)$$

Therefore the total heat flux through the interface vapour-liquid (q_{tot}) is

$$q_{tot} = q_\lambda + q_c. \qquad (14)$$

Equation (10), (12), and (13) have already been given by Colburn and Drew. Expanding the above by rearranging and introducing $k = \frac{D}{\delta_D}$, equation (10) yields

$$\frac{y_D - y_G}{x_G - y_G} = \frac{e^{\frac{N}{kC}} - 1}{e^{\frac{N}{kC}}} = 1 - e^{-\frac{N}{kC}}. \qquad (15)$$

If partial condensation is considered over a not too great range, the vapour line in the T–x diagram may be assumed to be straight, and if T' is the temperature of saturated vapour of a composition equal to x_G (see Fig. 3).

$$\frac{y_D - y_G}{x_G - y_G} = \frac{T_D - T_G}{T' - T_G}. \qquad (16)$$

From equations (15) and (16) follows after rearranging,

$$T_D - T_G = (T' - T_G)\left(1 - e^{-\frac{N}{kC}}\right). \qquad (17)$$

Substituting equation (17) in equation (12) and introducing $\frac{\lambda}{\delta_W} = h$, one obtains, because the Lewis number is taken, unity, and therefore

$$\frac{N}{kC} = \frac{N\,C_p}{h}:$$

$$q_\lambda = (T' - T_G)\,N\,C_p \qquad (18)$$

and therefore

$$q_{tot} = N\,(\Delta H)_{T_G} + N\,C_p\,(T' - T_G). \qquad (19)$$

$(\Delta H)_{T_G}$ is the enthalpy difference between saturated liquid and vapour at equilibrium at the temperature T_G. Introducing an enthalpy difference $(\Delta H)_{x_G}$ (see Fig. 3) between saturated liquid (T_G, x_G) and the saturated vapour of the same composition (T', x_G), equation (19) simplifies to

$$q_{tot} = N\,(\Delta H)_{x_G}, \qquad (20)$$

because (see Fig. 3): $(\Delta H)_{T_G}$

$$+ C_p\,(T' - T_G) = (\Delta H)_{x_G}.$$

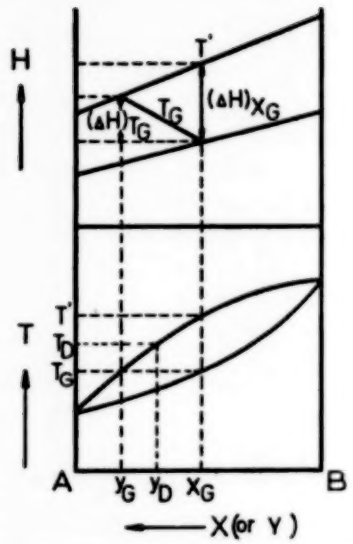

FIG. 3. Schematic representation of the enthalpy and boiling point as a function of the composition.

and it has been assumed, that $\bar{C}_p$ is constant over the temperature range involved.

For the condensation of a binary mixture the differential equation over a short height dz, under the conditions assumed, may therefore be written (see eq. 2)

$$(T_G - T_W)\,dz = \left(\frac{3\bar{\eta}\,\bar{M}}{\bar{\rho}^2 \cdot S \cdot g}\right)^{1/3} \cdot \frac{(\Delta H)_{x_G}}{S \cdot \bar{\lambda}} \cdot L^{1/3}\,dL. \qquad (21)$$

Introducing again a mean temperature difference between interface and wall defined by

$$(T_G - T_W)_m = \frac{1}{Z}\int_0^Z (T_G - T_W)\,dz,$$

and taking mean and constant values over the whole liquid film for ρ, η, λ and M and over the surface for $(\Delta H)_{x_G}$, integration of (21) yields

$$(T_G - T_W)_m = A_z L_Z^{4/3} \qquad (22)$$

in which $A_z = 1{,}082\,(\Delta H)_{\bar{x}_G} \cdot \frac{1}{Z} \cdot \left(\frac{\bar{\eta}\,\bar{M}}{\bar{\rho}^2\bar{\lambda}^3 S^4 g}\right)^{1/3}$.

For the vapour it has been found that :

$$T_D - T_G = (T' - T_G)\left(1 - e^{-\frac{N}{kC}}\right). \qquad (17)$$

Because only partial condensation will be considered over a rather small range of concentrations, $(T' - T_G)$ can be taken as fairly constant over the whole pipe. The same holds for k. The amount of vapour condensing N will be determined by q_{tot}, which in turn will be determined by the overall coefficient of heat transfer for the whole apparatus and the temderature difference between vapour and cooling fluid. For the condensation experiments to be described below, a liquid was used as a cooling fluid. Comparing the resistance in the cooling liquid with that in the condensing vapour, it can be concluded that here the greatest resistance against heat transfer was in the cooling liquid. Therefore the overall heat transfer coefficient will but slowly decrease from the top of the pipe to the underside. Moreover, the temperature difference between liquid and vapour was increasing somewhat from top to bottom, therefore the product of overall coefficient and temperature difference, that is q_{tot}, can in approximation be taken as constant. Therefore N is constant over the whole tube and equal to $N = \frac{L_Z}{S \,.\, Z}$. This leads to the conclusion that $T_D - T_G$ is constant for the whole tube.

The mean temperature difference between vapour and wall $\overline{\Delta T} = (T_D - T_W)_m$ therefore is

$$\overline{\Delta T} = (T' - T_G)\left(1 - e^{-\frac{L_Z}{S \cdot Z \cdot k \cdot C}}\right) + A_z L_Z^{4/3} \qquad (23)$$

Assuming that the mean composition of the liquid film at height z is $\bar{x}$, a material balance over the element dz gives

$$d(\bar{x}L) = x_G\,dL.$$

As $L = NSz$, because under the condition assumed N is constant over the whole length of the tube, the equation gives

$$d(\bar{x}z) = x_G\,dz,$$

from which follows $\bar{x}_Z \,.\, Z = \int_0^Z x_G\,dz$.

As $\bar{x}_G$ can be defined by $\bar{x}_G = \frac{1}{Z}\int_0^Z x_G\,dz$, it follows that

$$\bar{x}_G = \bar{x}_Z. \tag{24}$$

In other words, the mean composition of the liquid film at its surface is equal to the mean composition of the liquid leaving the apparatus. If it is wanted to check the relation found in equation (23), this can be most easily done at constant $\bar{x}_G$ (or what is the same, at constant $\bar{x}_Z$) and therefore constant $(T' - T_G)$.

As the ratio $\frac{\bar{\eta}\,\overline{M}}{\bar{\rho}^2 \cdot S^4 \cdot g \cdot \bar{\lambda}^3}$ (see eq. 22) for benzene and for toluene is practically the same, it has been assumed that this is also true for their mixtures. Therefore A_x is only a function of $(\Delta H)_{x_G}$. Under the assumptions made, the enthalpy as a function of the composition is a straight line. Therefore

$$A_x = A_A \bar{x}_G + A_B (1 - \bar{x}_G). \tag{25}$$

At constant $\bar{x}_G$, also A_x is therefore constant. The curve of $\overline{\Delta T}$ versus $L_Z^{4/3}$ (eq. 23) at constant $\bar{x}_G$ (or $\bar{x}_Z$) will therefore depend only on k, because for a fixed pressure C is constant. For $k = \infty$ the system will behave as an unair system. Equation (23) then simplifies to

$$\overline{\Delta T} = A_x \cdot L_Z^{4/3}, \tag{26}$$

the Nusselt equation, as could be expected. For $L_Z = \infty$, as $e^{-\infty} = 0$, equation (25) simplifies to

$$\overline{\Delta T} = T' - T_G + A_x L_Z^{4/3}. \tag{27}$$

All the curves for values of k between 0 and ∞ will have equation (27) as an asymptote. In Fig. 4 the form of several curves for a fixed $\bar{x}_G$ and therefore $T' - T_G$ has been drawn.

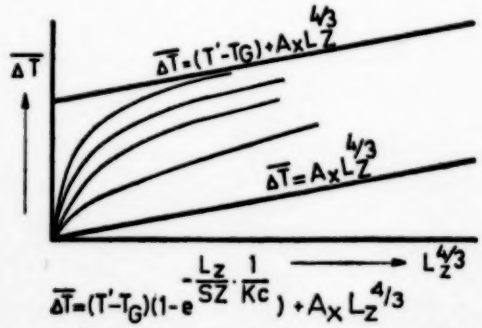

Fig. 4. Schematic representation of the equations (23), (26) and (27) at constant x_G.

Experimental

To check the above considerations, the condensation of a mixture of benzene and toluene has been carried out. The principle of the measurement was as follows (see Fig. 5).

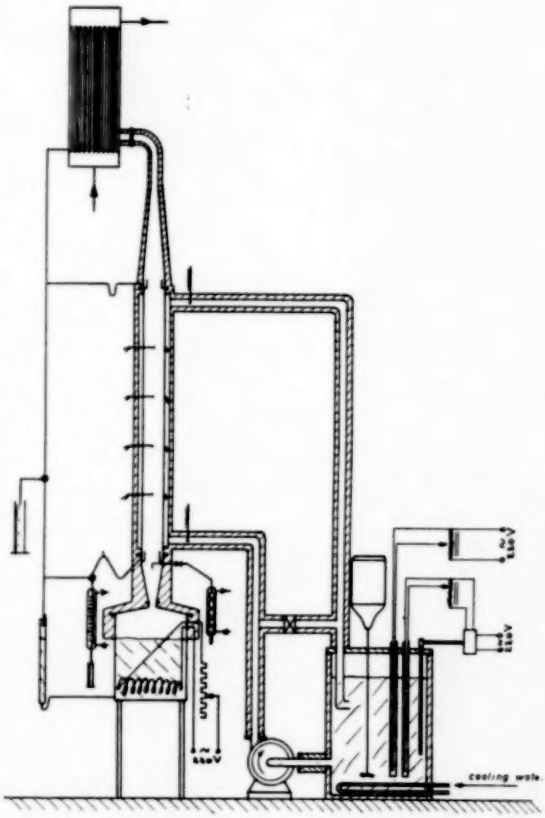

Fig. 5. The apparatus.

A vapour was generated in a cylindrical boiler by electrical heating of the liquid and introduced at the bottom of the inner cylindrical tube (diameter : $2R$: 88 mm, height Z : 1080 mm) of a double pipe condenser. The wall of the inner tube was 3 mm thick. The vapour was partially condensed by means of a cooling liquid (a lubricating oil of low viscosity) introduced tangentially in the outer pipe. The vapour which did not condense on the inner pipe was liquified in a total condenser cooled with water. The liquid formed here was collected, its quantity measured, and returned to the boiler. The condensate formed in the experimental condenser was collected, brought outside the apparatus, its quantity measured, and returned to the boiler. The cooling liquid

was pumped through the apparatus and was kept at a constant temperature by passing it through a thermostat. Eight copper-constantane thermocouples were installed in the apparatus, four in the centre of the inner condenser tube (vapourcouples), four in the wall of this condenser tube (wall couples). The e.m.f. of these thermocouples was measured with a Dieselhorst compensator with five decades. The accuracy of the measurement was 0, 5 μ V (corresponding with about 0·02°C).

Samples of the vapour entering the experimental condenser could be drawn via a side tube by total condensation. The pipeline connecting the two condensers was isolated, but no electrical heating to prevent condensation was applied. The condensate formed here was collected before it could enter the experimental condenser and was added to the product of the total condenser.

At intervals samples were drawn from the streams entering and leaving the experimental condenser, and these were analysed. After analysis the samples were returned to the boiler.

A careful calibration as well as recalibration at intervals of a few months of the thermocouples used was necessary. This calibration has been carried out as follows.

The vapour couples, which were easily detachable from the apparatus, were calibrated in the vapours of pure boiling liquids. The liquids and the constants used were:

	boiling point °C at 76 cm Hg	dT/dP, °C/mm Hg.
acetone	56·131	0·0386
methanol	64·65	0·035
benzene	80·122	0·0426
water	100·000	0·037
toluene	110·606	0·046

The fixed wall-couples were calibrated in the apparatus on the vapour couples. For this purpose boiler and total condenser were detached from the experimental condenser, the ends of which were closed with a flange. The whole condenser was very heavily isolated, whilst the top was also heated electrically to compensate for heat loss through the beams from which the apparatus hung. During at least 5 h, oil of a constant temperature was pumped through the annulus of the experimental condenser until the vapour couples all had constant and the same temperature (deviation of 0·05°C). The mean of these was taken as the actual temperature. The wall couples were read at the same time, and reading was continued over a rather long period. At least 20 readings were taken for each couple. The mean of these with a maximum deviation of 3 μV was taken, and assumed to be the same temperature as the vapour couples. The calibration of the wall couples was carried out at the temperatures 70, 80, 95 and 110°C. The calibrations were in every case evaluated in lines of the form

$$E = aT + bT^2.$$

In the apparatus the condensation of benzene and toluene and their mixtures has been measured. The compositions of the binary mixtures were measured by means of a semi-micro boiling point apparatus. The accuracy was 0·2%.

The results for benzene and toluene are represented in Fig. 6 with $\overline{\Delta T}$ in °C and L_Z in moles/sec.

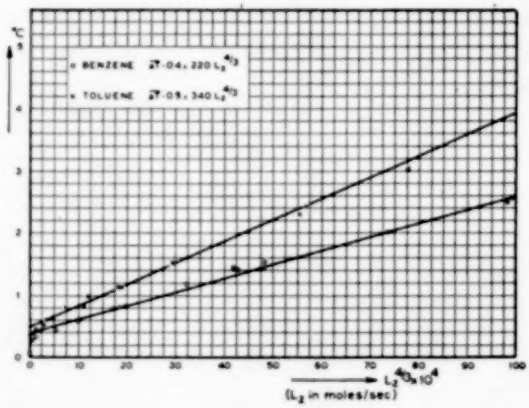

FIG. 6. The results of the condensation experiments with benzene and toluene.

Excluding the observations at very low amounts of condensate the measurements can be correlated by the equations

$$\overline{\Delta T} = 0{\cdot}4 + 220\,L_Z^{4/3} \quad \text{for benzene,}$$

$$\overline{\Delta T} = 0{\cdot}5 + 340\,L_Z^{4/3} \quad \text{for toluene.}$$

The straight lines do not pass through the origin as is demanded by theory. The cause of this seems to be that the amount of thermocouples used is too small, and moreover that the wall couples are not all well placed, causing a changing and too high a temperature difference for the larger amounts of condensate.

The theoretical slope of the lines can be calculated with the aid of equation (3).

The factor A has been calculated from the physical constants available and determined for benzene at 79°C, for toluene at 109°C, because

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the temperature difference between wall and vapour is 3°C at a maximum.

The following table gives the constants used.

	Benzene		Toluene		
(ΔH)	7370		7960		cal/mole
λ	3·5	10^{-4}	3·34	10^{-4}	cal/°C cm.sec
η	3·25	10^{-3}	2·55	10^{-3}	g/cm. sec
ρ	0·815		0·783		g/cm^3
M	78		92		g/mole
$\therefore A$	185		210		°C/(moles/sec)$^{4/3}$

As can be seen, the differences in slope between the calculated and determined lines are appreciable. This may be due to inaccuracies in the constants used and to deviations from physical behaviour assumed.

The experimental values as found will be utilized to evaluate the results of the condensation of the binary mixtures for which the same benzene and toluene has been used, and therefore will be used as a calibration of the apparatus. For the binary mixture two sets of experiments has been carried out, the first with a vapour containing 0·47 mol fraction of benzene, the second with a vapour containing 0·75 mol fraction of benzene. The vapour velocities and the temperature of the cooling liquid were varied.

In the first series, $\bar{x}_Z$ ranged from 0·490 to 0·268 (mean value 0·33). The mean vapour velocity $\overline{G}$ (in moles/sec) ranged from $G \cdot 10^3 = 4$ to 87, the Reynolds number of the vapour from 530 to 12070. In the second series $\bar{x}_Z$ ranged from 0·692 — 0·0,551 (mean value 0·61), $\overline{G} \cdot 10^3$ from 18 — 92 and the Reynolds number of the vapour from 1050 to 12360.

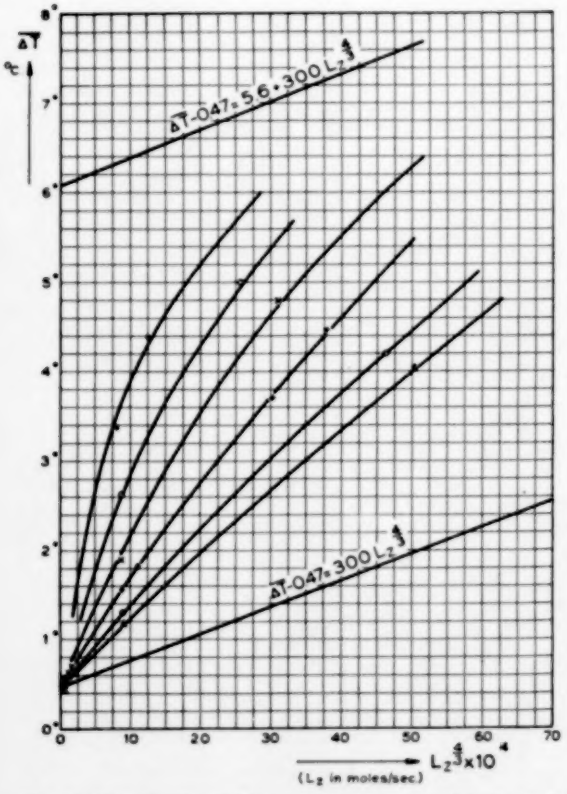

FIG. 7. The results of the condensation experiments with a mixture of benzene and toluene (series I, $\bar{x}_Z = 0{\cdot}33$).

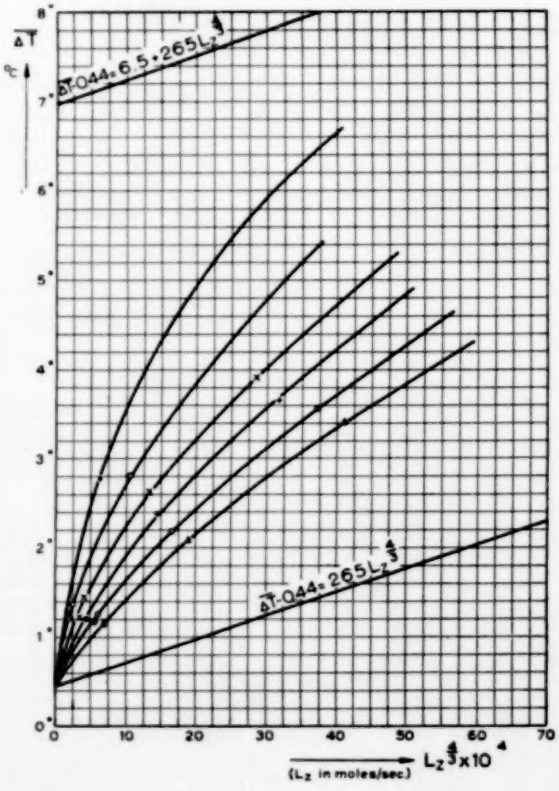

FIG. 8. Idem (series II, $\bar{x}_Z = 0{\cdot}61$).

Although the values for $\bar{x}_Z$ differ rather considerably, also in each series, the differences in A_x (280 to 307 : mean 300 for series I and 256 to 274 : mean 260, for series II) as well as in $T' - T_G$, are of such a magnitude that a comparison of the values obtained within each series is permitted. The results have been plotted in Fig. 7 for series I, in Fig. 8 for series II. The values for about equal Reynolds numbers have been marked in the same way and have been combined. The lines drawn have been calculated for $\bar{x}_Z = 0{\cdot}33$ and $= 0{\cdot}61$ respectively and the corresponding $T' - T_G$ as read from the vapour-liquid equilibria data for benzene-toluene. The temperature differences are given in the figures as they have been found experimentally. The equations given in the figures for $k = \infty$ and $k = 0$ are corrected for the observed deviation in $\overline{\Delta T}$ of the pure substances (see the equations above).

As is clear from Figs. 7 and 8, the qualitative picture obtained is in agreement with Fig. 4 given in the theoretical part.

From the data collected it is possible to calculate k for each experiment, because $(T_D - T_W)$, $\bar{x}_Z$, and L_Z have been measured ; moreover A_x can be calculated from equation (27) and $T' - T_G$ read from the equilibrium curve. It can be found that :

$$k = \frac{L_Z/S \,.\, Z \,.\, C}{-\ln \dfrac{T' - T_G - \overline{\Delta T} + A_x \,.\, L_Z^{4/3}}{T' - T_G}} \qquad (28)$$

The form under the ln sign in equation (28) is the ratio of the vertical distance of the point plotted to the asymptote, and the vertical distance between this asymptote and the line for $k = \infty$. Therefore k is independent of the corrections mentioned before.

The values found for k have been plotted in Fig. 9 versus the Reynolds number of the vapour stream to the power 0·8. For turbulent flow in a pipe $Sh : (Re)^{0.8}\ (Sc)^{1/3}$. If it is assumed that D and $Sc^{1/3}$ are constant for the systems investigated, a straight line will be obtained in such a case.

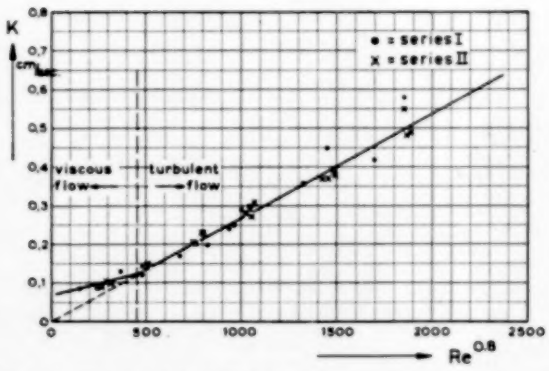

FIG. 9. The partial coefficient of mass transfer (k) as a function of $Re^{0.8}$.

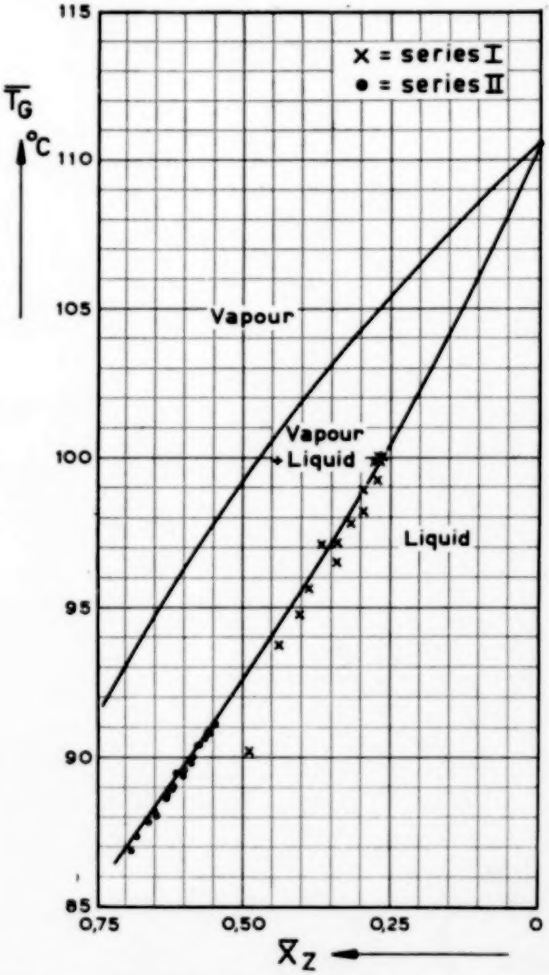

FIG. 10. The temperature $\overline{T}_G$ calculated from $\overline{T}_G = \overline{T}_W + A_x L_Z^{4/3}$ as a function of x_Z.

As can be seen from Fig. 9, this relation for the region of $Re > 2000$ ($Re^{0.8} > 450$) is fairly well satisfied.

Finally $\bar{T}_G$ has been calculated from the data obtained and plotted versus $\bar{x}_Z$ in Fig. 10, together with the lines for saturated liquids and vapours. Although most of the points lie below the line for the saturated liquids, the correlation is not too unsatisfactory.

Conclusion

Although the experimental results given are by no means sufficient, or absolutely conclusive, they indicate that the approach made can, in certain cases, be used for the calculation of the condensation of binary mixtures with sufficient accuracy.

Nomenclature

A	= constant in Nusselt's equation	°C/(mole/sec)$^{1/3}$
C	= molal concentration	moles/cm^3
C_p	= molal specific heat at constant pressure	cal/mole°C
c_p	= specific heat at constant pressure	cal/g °C
D	= diffusion coefficient	cm^2/sec
g	= acceleration of gravity	cm/sec^2
G	= vapour flow	moles/sec
ΔH	= molal enthalpy difference between vapour and liquid	cal/mole
h	= partial heat transfer coefficient	cal/°C cm^2 sec
k	= partial mass transfer coefficient	cm/sec
L	= flow of condensate	moles/sec
M	= molecular weight	g/mole
N	= amount of condensate, formed per unit of time and area	moles/cm^2 sec
n	= molal flux in r direction	,,
p	= molal flux in z direction	,,
q	= heat flux to the wall	cal/cm^2 sec
R	= radius of the tube	cm
Re	= Reynolds number of the vapour	no dimension
r	= coordinate in radial direction	cm
S	= circumference of the tube	cm
Sc	= Schmidt number of the vapour	no dimension
Sh	= Sherwood number of the vapour	no dimension
T	= temperature	°C
T'	= temperature of a saturated vapour of a composition equal to x_G	°C
ΔT	= temperature drop from vapour to wall	°C
x	= mole fraction of more volatile component in the liquid phase	
y	= mole fraction of more volatile component in the vapour phase	
z	= co-ordinate in vertical direction (measured from the top)	cm
Z	= length of tube	cm
Γ	= condensate flow per unit of circumference by volume	cm^3/cm sec
δ_L	= thickness of liquid film	cm
δ_D	= thickness of "laminar vapour film" related to diffusion	cm
δ_W	= thickness of "laminar vapour film" related to heat transfer	cm
η	= viscosity	g/cm sec
λ	= heat conductivity	cal/°C. cm sec
ρ	= density	g/cm^3

Subscripts

A	= lower boiling component
B	= higher boiling component
C	= condensation
D	= vapour
G	= interface
L	= liquid
λ	= conduction
x	= constant or mean composition
T	= constant temperature
Z	= bottom of the tube

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The j_H and j_D factor of air use for drying

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Abstract—Under constant drying conditions the j_H factor for heat transport and the j_D factor for mass transport have been determined for the drying air with four evaporating substances : benzene, carbontetrachloride, ethanol and water. It has been found that under the conditions mentioned substantially $j_H = j_D$, as wanted.

Résumé—Les auteurs ont déterminé, dans des conditions de séchage identiques, les facteurs j_H de transfert de chaleur et j_D de transfert massique, relatifs au séchage de l'air avec quatre agents d'évaporation benzène – tétrachlorure de carbone – éthanol et eau. Dans les conditions mentionnées ci-dessus, les expériences montrent l'égalité entre j_H et j_D comme prévue par la théorie.

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THE analogy between heat transfer and mass transfer, expressed e.g. in the equality of the j factor of CHILTON and COLBURN [1] for heat transfer j_H to that of mass transfer j_D for geometric equal cases, can be verified in an elegant manner in the case of simultaneous heat and mass transfer from one body (and therefore of exactly the same geometrical form) as occurs in drying a moist solid substance in a hot gas.

In particular, in the constant-rate period of drying under constant drying conditions of a porous nonshrinking body, the study of the validity of the equality mentioned for the drying gas is facilitated not only because the surface temperature is constant in this period, but also by the fact that the resistance to heat flow in the gas phase is large, compared with the resistance in the moist porous body. Therefore, during the constant-rate period of drying, not only the surface, but the whole body is at a fairly constant temperature, viz. the wet-bulb temperature of the drying air, because the differences in temperature in the body are within the error of determination if the bodies chosen are not too thick.* This facilitates the measurements, because in such a case this temperature can be actually measured under drying conditions, and need not be calculated. Based on this, the present authors have undertaken to measure the j_H and j_D factor for air of four liquids evaporating from a porous earthenware body, viz.: benzene, carbontetrachloride, ethanol, and water.

EXPERIMENTAL

The principle of the measurement used was that a stream of air of known temperature and humidity was passed over a moist porous earthenware bloc. The conditions chosen were such that the air, in drying, did not change appreciably in temperature and moisture content. The moist body suspended via a microburette filled with the liquid to be evaporated from one of the beams of a balance ; the amount of liquid evaporated was then found by differences in weight, as a function of the time. If the position of the whole setup is rigid enough towards horizontal movements, the current of air has no influence on the weight measured.

The setup with the microburette as given was chosen to lengthen the constant-rate period. The point of the burette was inserted into the porous body and the flow of liquid was adjusted in such a manner than it was about equal to the amount evaporated. To prevent an eventual fall of drops from the body, this was tightly wrapped in a rayon gauze. Bare blocs of an originally rectangular form of $2 \times 5 \times 10$ cm, slightly streamlined at the ends, were used. Besides the rate of evaporation, the dry-bulb temperatures of the body at several places were measured with thermocouples. Moreover, the difference of pressure in the measuring section with barometric pressure was determined with a differential manometer.

The air used was conditioned in the following manner (see Fig. 1). Moved by a blower, it was first saturated with vapour by passing it through a humidifying tower. After humidification, the air passed a condenser (cooled

* Experimental proof of this fact will be given on another occasion.

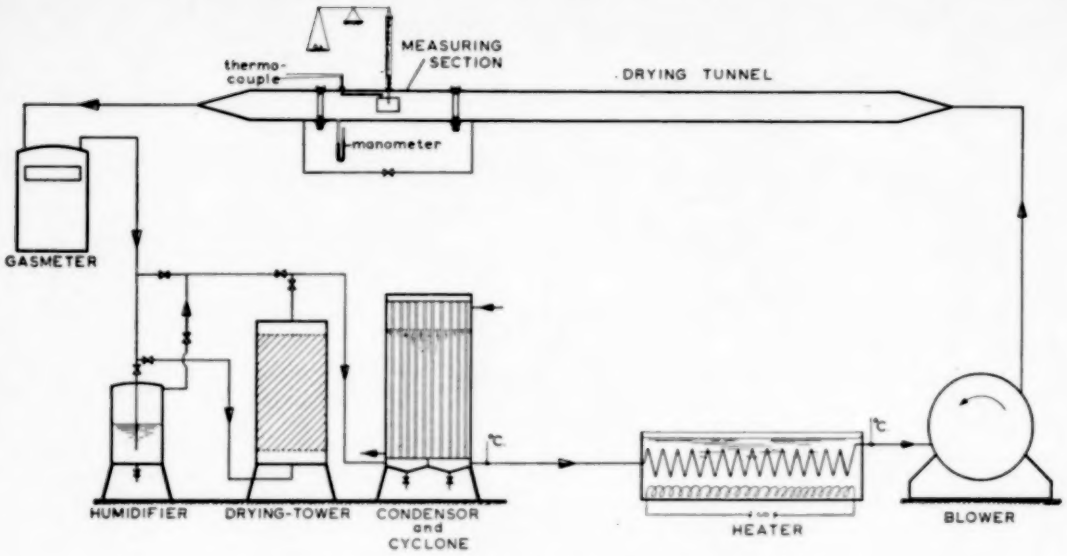

FIG. 1. Sketch of the drying apparatus.

with water at constant end-temperature lower than the temperature of the humidifying tower), and then a cyclone to catch liquid drops. In this way, air of a constant humidity (determined at constant speed by the temperature of the condenser) could be obtained. The wanted temperature of the air was then adjusted by passing the air through a regulated electrical heater, commanded by the entrance temperature of the tunnel. After passing the drying tunnel, the air re-entered the humidifying tower. During the measurements the humidifying tower was also bypassed. A closed-circuit apparatus had been chosen to prevent great losses of liquid and contamination of the atmosphere. If the measurements were carried out with the organic liquids, the air was first dried by means of silicagel contained in a tower in a bypass, before being conditioned. The dew point of the dry air was in all these cases 30°F. The metal drying tunnel consisted of a calming section and the actual measuring section made from copper tube. During conditioning the measuring section was bypassed, because it took about 2 hr to obtain a constant humidity and temperature of the air. The amount of air was measured with flow raters or a gas meter. The humidity was determined via the dew point with an apparatus as sketched in Fig. 2.*

The long leg of the apparatus was placed in a cooling medium, say liquid air, at a temperature far below the dew point to be measured. Therefore heat flows from the

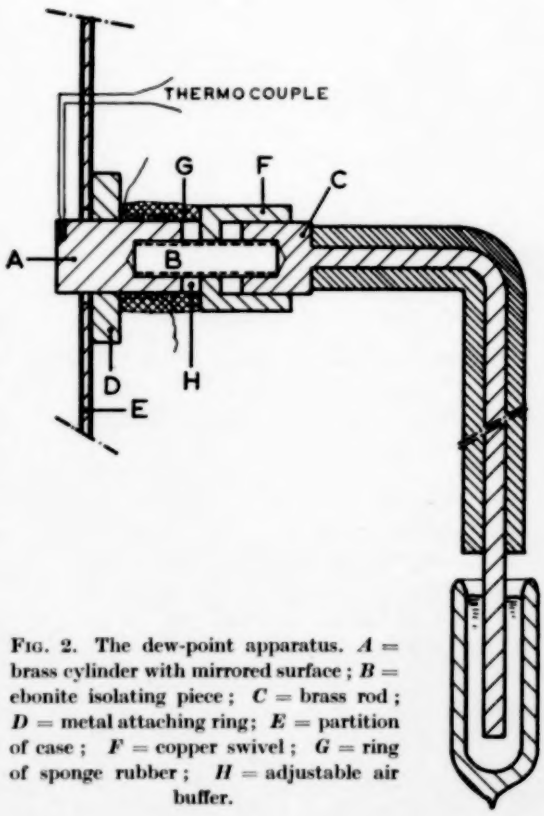

FIG. 2. The dew-point apparatus. A = brass cylinder with mirrored surface; B = ebonite isolating piece; C = brass rod; D = metal attaching ring; E = partition of case; F = copper swivel; G = ring of sponge rubber; H = adjustable air buffer.

* The apparatus has been developed in this laboratory by C. VAN DER SPOEL and C. HUYGEN on a principle put forward by Ir. G. VAN TOL of the Philips Laboratories at Eindhoven.

small cylindrical body A of the apparatus, and as soon as its surface has reached a temperature below the dew point of the surrounding air, amongst others a condensate will be formed on the mirrored surface of the apparatus. A beam of light falling on a photoelectric cell via this mirror will then be diffused.

The interceptance of the beam of light puts in action a relay, working on the photocell, by which an electrical circuit, in which a small heating element surrounds the cylindrical body, is closed. The temperature of the body therefore rises and the condensate disappears from the surface, upon which the heating stops. The process described will then repeat with ever smaller and smaller differences in temperature of the cylindrical body. The mean temperature of the body (measured with a small thermocouple or with a thermometer) will approach the dew point of the surrounding air. The apparatus gives dew points with an accuracy of about 0·1°F. However, the time to reach equilibrium with sufficient accuracy is rather long, (15 minutes) and the instrument therefore can only be used when working under stationary conditions. As a typical example, in the following Table 1, for one experiment chosen at random, the temperatures involved are given as a function of the time during stationary experimental conditions. T_1 and T_2 represent the temperature at two places in the body. T_D is the dry-bulb temperature of the air.

Table 1.

	0	15′	35′	80′	110′
T_1°C	31·7	31·8	31·8	31·6	31·9
T_2°C	31·6	31·7	31·6	31·5	31·6
T_D°C	47·9	47·8	47·8	47·9	47·7
Dewpoint °F	82	82	82	82	82

The wet-bulb temperature (T_{wb}) of the air measured in a small quantity of liquid in the drying tunnel was 31·7°C and therefore equal to the temperature of the body.

Method of Calculation and Results

From the amount of liquid evaporated as a function of the time the rate of evaporation ϕ_m can be calculated. The rate of heat transfer ϕ_H is therefore : $\phi_H = \phi_M \, \Delta W$, in which ΔW is the enthalpy difference between the vapour at the temperature T_D and the liquid at the temperature T_{wb}. The partial coefficient of mass transfer (k) and heat transfer (h) can then be calculated with the aid of the equations :

$$\phi_H = h\,(T_D - T_{wb}) \qquad (1)$$

$$\phi_M = \frac{k}{RT}(p_{wb} - p_g). \qquad (2)$$

It has been assumed that in the correlation $\mathrm{Nu} = c\,(Re)^m\,(Pr)^n$ and $\mathrm{Sh} = c\,(Re)^m\,(Sc)^n$ the exponent $n = \frac{1}{3}$, because under the prevailing circumstances the air velocity at the interface gas body can be assumed to be zero [2].* Therefore for j_H and j_D the original definitions of Chilton and Colburn could be used.*

$$j_H = (Nu)\,(Re)^{-1}\,(Pr)^{-1/3} = \frac{h}{c_p\,\rho\,V}(Pr)^{2/3} \qquad (3)$$

$$j_D = (Sh)\,(Re)^{-1}\,(Sc)^{-1/3} = \frac{k}{V}(Sc)^{2/3} \qquad (4)$$

The properties of the mixtures necessary to evaluate equations (3) and (4) have been calculated, if need be, for a mean temperature $T = \frac{T_D + T_{wb}}{2}$, and for the pressures measured and based on numerical data taken from the literature.

For the diffusion coefficient and the Schmidt number the collected data of Sherwood and Pigford [3] have been used. For the heat of evaporation, the vapour pressures, the density and the viscosity, several sources [4] have been consulted.

It has moreover been assumed that the density, the specific heat, and the Prandtl number were additive for the mixtures. The velocity V has been taken as the superficial gas velocity, therefore calculated on the empty tunnel.

Finally, the attention may be turned to the fact that the factor h has not been corrected for heat transported by radiation from the surroundings to the bloc, as follows from the equation given. Under the conditions chosen this amount of heat is small compared with the heat transported by conduction and convection. Moreover, the calculation of this amount gives an approximate figure only. The influence of the radiation can be measured by comparing the h factor with an analogous factor (h_r) for radiation. This partial coefficient of heat transfer by radiation can be calculated by means of the equation

* The present authors are of the opinion that in general the j factor should be defined by : $j_H = Nu\,Re^{-1}\,Pr^{-n}$ and $j_D = Sh\,Re^{-1}\,Sc^{-n}$, n ranging from $\frac{1}{3}$ to $\frac{1}{2}$.

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$$h_r = \sigma(4T_m^3) \Big/ \left[\frac{1}{\epsilon_b} + \frac{A_b}{A_w}\left(\frac{1}{\epsilon_w} - 1\right)\right]. \qquad (5)$$

In this equation, which is valid for small temperature differences betwene the source and sink (see e.g. ARNOLD [5]), T_m denotes the arithmetic mean temperature of wall and bloc ; ϵ_w and ϵ_b are the emissivities, and A_w and A_b are the surfaces of wall and bloc respectively. The constant σ has the value : $5{\cdot}73\ 10^{-8}$ joules/m^2 sec (°K)^4.

In the case investigated the ratio $A_w/A_b \sim 2$, therefore the emissivity of the wall has a large influence on h_r, and because the emissivity of the red-copper polished wall is small, h_r will consequently be small.

Introducing e.g. in equation (5) for T_m : 313°K, for $\epsilon_b = 0{\cdot}9$; for $\epsilon_w = 0{\cdot}06$, the value of $h_r = 0{\cdot}7$ Joules/m^2 sec °C.

When h_r is compared with the values found for h (60-27), and the accuracy of the measurements seen, the conclusion is warranted that correction of h (about 2%) is not necessary and not justified. It may be emphasized that, as has been demonstrated by ARNOLD (*l.c.*) the amount of heat transported by radiation, even for small temperature differences between source and sink, cannot always be neglected, in particular if the body to which heat flows is small compared with the radiating walls.

The results obtained are collected in Table 2. As can be seen, the variation in the ratio j_H/j_D in the various experiments is rather large. However, no dependence of the Reynolds number can be traced, as can be found by plotting j_H/j_D versus the Reynolds number. It seems therefore safe to calculate a mean value for every system. These values have been included in the table.

Including the uncertainty caused by some of the data used in the calculation, in particular with regard to the diffusion coefficients and the Schmidt number, it can be concluded that, for the regions and systems investigated, the assumption $j_H = j_D$ is valid.

Correlation of the j factor with the Reynolds number takes the form

$$j = c\,(Re)^{m-1} \qquad (6)$$

Plotting $\log j$ against $\log Re$ (Re calculated for the air in the empty tube), as has been done in Fig. 3, enables to calculate c and m by the method of least squares. It appears that $c = 0{\cdot}45$ and $m = 0{\cdot}62$. It may be observed that in Fig. 3 some experiments with naphthalene have also been included. These experiments have been carried out with blocks of pure naphthalene, shaped in the same fashion as the earthenware bodies. Only the j_D factors could be included because the differences in $T_d - T_{wb}$ are too small (0·3°C) to enable the calculation of j_H with enough accuracy.

Comparison of the data obtained with the many found in the literature [3, 6] based on j_D, j_H, or j do not seem appropriate. It would only add to the confusion in this field. The more so,

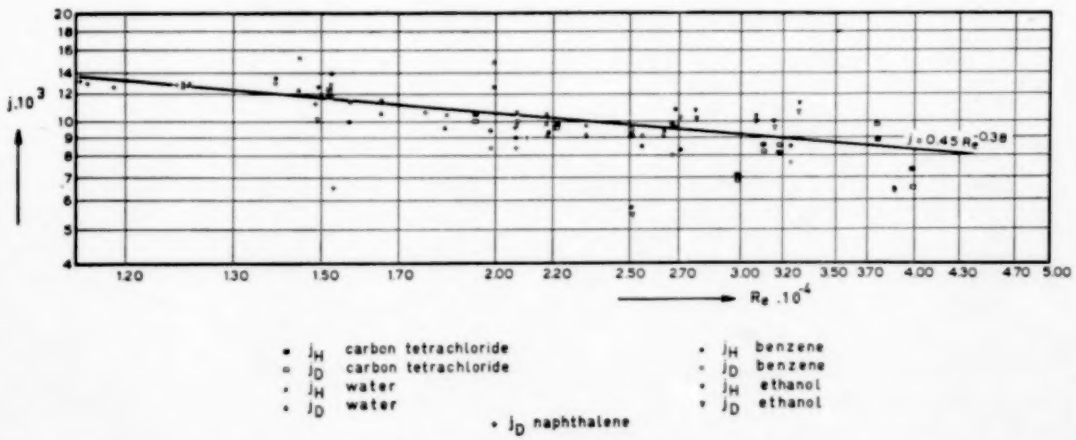

FIG. 3. Log j as a function of log Re.

Table 2.

Water	$Re \times 10^{-3}$	$\bar{v}$	$k \times 10^2$	h	$j_H \times 10^3$	$j_D \times 10^3$	j_H/j_D
H	18·4	3·05	4·12	47·8	10·5	9·6	1·09
J	12·5	2·03	3·66	40·5	13·3	12·8	1·04
K	21·8	3·54	4·94	57·9	10·7	9·9	1·08
L	23·5	3·82	4·84	56·4	9·7	9·0	1·08
M	14·2	3·97	3·97	55·2	15·6	12·2	1·28
N	16·7	2·72	4·14	49·6	11·9	10·8	1·10
a	15·2	2·43	4·83	46·4	13·0	14·1	0·92
b	19·9	3·18	6·73	60·6	12·9	15·0	0·86
c	26·5	4·22	5·40	58·4	9·4	9·1	1·03
							mean : 1·1
Carbontetrachloride							
1	39·7	3·15	1·23	37·8	7·3	6·5	1·13
2	31·6	2·15	1·29	34·4	8·2	8·5	0·96
3	15·5	1·21	0·92	24·4	12·0	12·6	0·95
4	18·9	1·54	1·01	26·5	10·5	10·1	1·04
5	25·1	1·98	1·12	31·3	9·2	9·4	0·98
6	22·2	1·77	1·02	30·0	9·8	9·6	1·02
7	29·8	2·45	1·01	28·3	6·9	6·8	1·02
8	31·3	2·67	1·32	35·3	8·5	8·2	1·04
9	38·7	3·11	1·84	47·0	8·7	9·8	0·89
							mean : 1·0
Benzene							
1	26·5	3·08	1·73	35·0	9·8	8·0	1·22
2	21·9	2·49	1·59	29·6	9·3	9·2	1·02
3	26·8	3·01	2·04	42·8	10·9	9·7	1·12
4	38·3	4·27	1·90	36·0	6·4	6·4	1·01
5	32·3	3·62	1·93	40·1	8·5	7·6	1·11
6	27·1	3·04	2·18	32·8	8·3	10·2	0·81
7	25·7	2·90	1·85	31·9	8·5	9·1	0·94
8	19·8	2·25	1·33	27·2	9·4	8·5	1·11
9	15·9	1·78	1·46	23·4	10·1	11·7	0·86
10	14·1	1·61	1·56	27·6	13·3	13·8	0·97
11	20·5	2·32	1·61	27·0	9·0	9·9	0·91
							mean : 1·0
Ethanol							
1	20·5	2·64	2·22	26·4	10·9	10·0	1·09
2	30·7	3·96	3·33	28·2	10·5	10·0	1·05
3	25·3	3·26	1·74	16·8	5·6	5·4	1·04
4	28·2	3·63	3·13	36·2	10·9	10·3	1·06
5	14·8	1·91	1·62	23·3	13·3	10·1	1·32
6	33·2	2·47	2·23	26·6	11·7	10·7	1·09
7	31·7	4·09	3·47	35·9	10·1	9·6	1·06
							mean : 1·1

since the Reynolds number used has not been based on the correct parameters. First the superficial velocity has been used and not a velocity with respect to the surface of the block. Secondly, the diameter of the drying section has been taken instead of a length parameter from the body. The rather peculiar shape of the body prevented the authors from doing so with any amount of

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certainty. Therefore, the only conclusion of some importance to be drawn from Fig. 3 is that it indicates that equation (6) seems to be fulfilled, for the conclusion of which the figure has been presented, and that $m = 0{\cdot}62$ for the form given. Any change in the velocity or the length parameter, which will be relatively the same for every experiment, does not change this conclusion.

Conclusion

Under the experimental conditions given, the equality of the j_H and the j_D factor for the gas phase seems fairly well satisfied.

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Nomenclature

A = surface	m^2
ϕ_m = rate of mass transfer	moles/m^2 sec
ϕ_H = rate of heat transfer	Joules/m^2 sec
T_{wb} = wet bulb temperature of the air	°C
T_D = dry bulb temperature of the air	°C
W = enthalpy	Joules/mole
h = partial coefficient of heat transfer	Joules/m^2 °C sec
h_r = partial coefficient of heat transfer by radiation	Joules/m^2 °C sec
k = partial coefficient of mass transfer	m/sec
j_H = j factor for heat transfer	no dimension
j_D = j factor for mass transfer	no dimension
V = linear velocity of the gas	m/sec
p_{wb} = partial vapour pressure of vapours in equilibrium with liquid of temperature T_{wb}	atm
p_g = partial vapour pressure of vapours in equilibrium with liquid of the dewpoint	atm
Nu = Nusselt number $\left(\frac{hD}{\bar{\lambda}}\right)$	no dimension
Re = Reynolds number $\left(\frac{V\rho D}{\bar{\lambda}}\right)$	no dimension
Pr = Prandtl number $\left(\frac{c_p\bar{\eta}}{\bar{\lambda}}\right)$	no dimension
Sc = Schmidt number $\left(\frac{\bar{\eta}}{\bar{\rho}Diff}\right)$	no dimension
Sh = Sherwood number $\left(\frac{kD}{Diff}\right)$	no dimension
Le = Lewis number $\left(\frac{\bar{\lambda}}{\bar{\rho c}_p\, Diff}\right)$	no dimension
D = diameter of tube	m
η = viscosity	Kg/m sec
λ = thermal conductivity	Joules/m °C sec
c_p = specific heat at constant pressure	Joules/°C kg
$Diff$ = diffusion coefficient	m^2/sec
ρ = density	Kg/m^3
ϵ = emissivity	no dimension
σ = constant	Joules/m^2 sec(°K)^4

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Separation of m-cresol and p-cresol by extractive crystallization

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Abstract—The principles of the new separation method, called " Extractive Crystallization " are described in detail. This new method has been applied for the separation of cresol mixtures, using acetic acid as the extractive crystallization solvent. The results obtained show that this new process can serve as a useful method of separation in the presence of a suitable solvent.

Résumé—Les auteurs décrivent en détail les principes d'une nouvelle méthode de séparation nommée " cristallisation extractive." Ils ont appliqué cette nouvelle méthode à la séparation de mélanges de crésols en utilisant l'acide acétique comme solvant d'extraction.

Les résultats obtenus montrent que ce procédé peut servir utilement pour la séparation en présence de solvant approprié.

Introduction

One of the most frequently occurring problems in the field of chemical engineering is the separation of the components of a mixture. There are available several general techniques such as fractional distillation, azeotropic or extractive distillation, and liquid-liquid extraction, whereby such a separation may be brought about. If the components of a mixture, however, have comparable volatility and close chemical properties so that no selective agent can be found for facilitating their separation, none of the above methods will be applicable or economic for their separation.

The mixture of *m*- and *p*- cresols is such an example. Various attempts made in the past to separate them from their mixtures by extractive or azeotropic distillation have not met with any success [14]. These components have been, however, resolved by other methods. The commonest method employed is that of treating the mixture with a foreign agent which forms *addition compounds* with the individual components. The foreign agent is so chosen that either a compound is formed with only one of the components or, if the compounds are formed with both the components, they may have different physical properties, with the result that they can be separated by any of the common methods of separation including fractional crystallization. For example, Bentley and Catlow [1] used benzidine as a foreign agent which formed addition compounds with cresols, and these were then separated by cooling the mixture to a temperature of 95°C (when the *p*-cresol addition compound crystallized out) and subsequent filtration. Savitt and Othmer [15] washed the benzidine addition compound cake free of entrained mother-liquor with an inert solvent (benzene), and improved the purity of the product from 85% as obtained by Bentley and Catlow (*loc. cit.*) to 98%. Among the other agents employed the following may be mentioned : phenol [10], nitrous acid [8], urea [17], hexamethylene tetramine [3], 4-picoline [3] and oxalic acid [7]. The second method employed is to prepare suitable *derivatives*. which are easily separable and then the original compounds won back from them. For instance, *m*- and *p*-cresols were converted into their respective sulphonic acids which were then separated, taking advantage either of their differential solubility in water or of the difference in the temperature at which they hydrolysed [2]. The cresols were also separated by debutylation [19], of the butylated derivatives. On a laboratory scale, cresol mixtures were also separated by liquid-liquid extraction using a buffered solution having a *p*H of 10·8 as the extracting solvent [4].

An entirely physical method of separation of such mixtures into their components is possible if the components form eutectic mixtures without the formation of solid solutions. For, in absence of the formation of solid solutions, one of the

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components (with only a negligible amount of the other component) crystallizes out on cooling till the eutectic temperature is reached. The separation realizable by such a simple freezing process, however, is limited by the composition of the eutectic mixtures. However, if the crystallization is carried out in presence of a third agent (solvent) which forms single eutectic systems with either of the feed components, the further separation of the components may be possible, and particularly so if the ternary eutectic composition is shifted in a favourable direction.

A process of separation of *m*- and *p*-cresols based on this method (termed hereafter "extractive crystallization"), using acetic acid as the foreign solvent, was tried out, and the present paper incorporates the theoretical considerations of the above process and the solid-liquid phase equilibrium data for the ternary system *m*-cresol–*p*-cresol–acetic acid.

The term "extractive crystallization" has also been used by previous workers to describe some of the methods [17] mentioned earlier. However, it is felt that this term should exclusively be used for a process in which the separation of components themselves is effected by crystallization in presence of a solvent.

Theoretical Considerations

For discussing the principles underlying the process of extractive crystallization, consider a ternary system of components ***A***, ***B***, and ***C***, of which ***B*** and ***C*** are the feed components to be separated from each other and ***A*** is the foreign agent. Let this be the simplest possible ternary system, viz. the system in which the corresponding binaries are all single eutectic systems and in which no solid solutions are formed. The nature of the solid-liquid equilibrium diagram for such a system will be as shown in Figs. 1 (a) and 1 (b). Fig. 1 (b) consists of a concentration triangle ***ABC*** with the three binary diagrams laid out along its sides.

In these diagrams, ***FL*** (or ***F'L***), ***KL*** (or ***K'L***) and ***HL*** (or ***H'L***) are the binary crystallization curves, and they trace out the concentration regions ***AF'LK'A***, ***BH'LF'A*** and ***CKLH'C*** (see Fig. 1 (b)) in which the components ***A***, ***B*** and ***C*** will precipitate out in nearly pure forms during primary crystallization range. The point ***L*** is the ternary eutectic point, and its composition represents the limit of separation in an extractive crystallization process. It is evident from these diagrams that if the composition of the overall mixture is such that it lies in either of the two

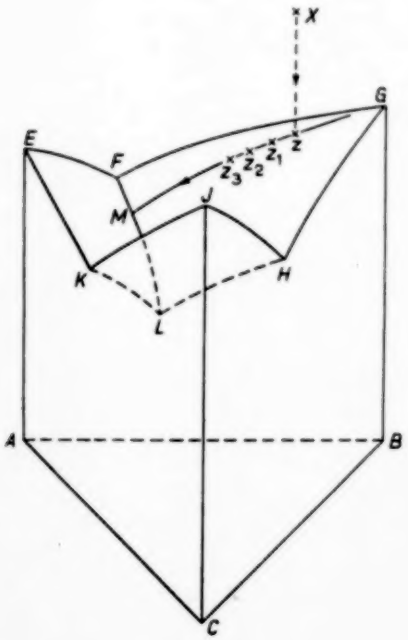

Fig. 1 (a).

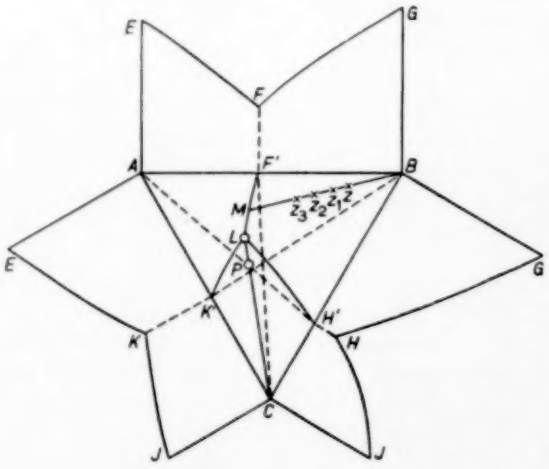

Fig. 1 (b).

triangles $K'LC$ or $H'LB$, both in the primary as well as the binary crystallization regions, only one of these components and/or the solvent will crystallize out, and if the crystallization process is arrested just before the ternary eutectic point is reached, the solid phase will consist of only the solvent and one of the feed components, while the liquid phase will contain all of the other feed component together with the balance amount of the solvent and the crystallizing feed component. On the other hand, if the overall composition of the mixture, to start with, is such that it lies on either the line CL or BL, right up to the eutectic point, only one component (either C or B) will crystallize out, and from the practical point of view it would be advantageous to work with such mixtures. The diagram also reveals that, if the disposition of the ternary eutectic L is favourable, the binary eutectic mixtures between B and C can be further treated for the separation of either B or C in the pure form. For example, a required amount of A may be added to the mixture H so that a ternary mixture of the composition represented by a point P lying on the line CL is obtained which on cooling will precipitate out the component C right up to the ternary eutectic temperature.

The above considerations also apply for a ternary mixture in which one of the three binaries

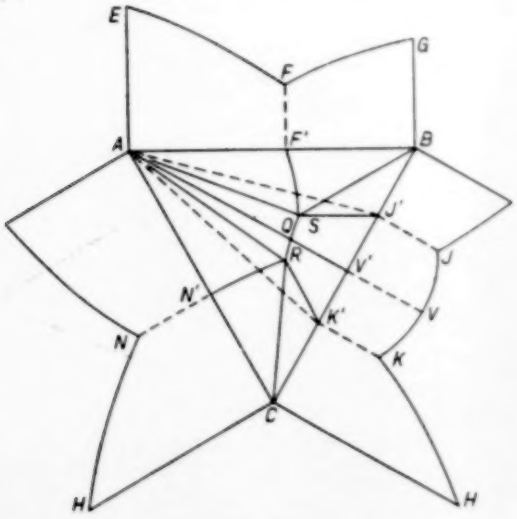

Fig. 2.

is a two-eutectic system accompanied with a compound formation as is the case in the *m*-cresol–*p*-cresol–acetic acid system. In such a case, as is indicated in Fig. 2, there will be two ternary eutectics, R and S. The point Q lying on the line $V'A$ (where V' is the composition of the binary compound between B and C) may be regarded as the eutectic of the pseudobinary system between V' and A. If it is intended to separate B from C, the concentration region $CRSBC$ should be avoided. The two ternary minimum points, instead of lying in two different triangles (AVB and AVC), may also lie in one of them only, as indicated in Fig. 3. In such a case, only one of them is a true ternary eutectic, while the other is called a peritectic point. Besides these peritectic type of systems, other types of systems with solubility gaps in either the liquid or solid phase are also possible, but are not discussed here as the solid-liquid phase equilibrium diagram for the system studied does not belong to any of them.

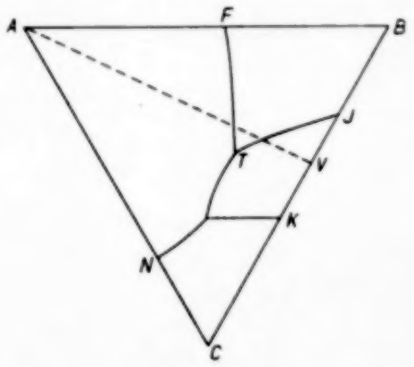

Fig. 3.

Experimental

Materials

Cresols—During the investigation, B.D.H. quality cresols (reported as 98-100% pure) were used after distillation in a column packed with glass helices (equivalent to twelve theoretical phates). Only the middle cut of the fraction distilling over in the temperature range of 201-202°C was used, which usually had the following constant melting points for the two cresols: *m*-cresol 11·50°C, and *p*-cresol 34·5°C.

Acetic acid—The Merck quality acetic acid was first refluxed for about two hours with a calculated amount of acetic anhydride, and thereafter the middle cut of the

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fraction distilling over at 118°C was collected and had a melting point of 16·5°C.

Determination of binary solid-liquid equilibrium diagrams

The apparatus for the measurement of disappearance points consisted of a freezing point tube of about 1¼ in. in diameter which carried a mechanical stirrer and an accurately calibrated thermometer. About 25 g of the mixture of a known composition was charged into it, and thereafter it was surrounded by an unsilvered vacuum flask (about 4 in. i.d.) which carried an alcohol-solid carbon dioxide freezing mixture. The distance between the bottom of the tube and the surface of the mixture determined the rate of cooling. Where supercooling with the mixture was excessive, it was necessary to freeze the whole mixture and then warm it slowly by taking it away from the freezing mixture, this being effected by the lowering of the Dewar flask. The warming rate was adjusted to about 0·5-1·0°C a minute to enable the accurate determination of disappearance points. The whole mixture was illuminated by an electric bulb outside the Dewar flask to enable careful observation of either the disappearance or appearance points. (Appearance points could only be determined with acetic-acid-rich mixtures.) For each mixture, the process was repeated three or four times and the mean value of the readings was taken as the correct temperature at which the phase change occurred. The solid-liquid phase equilibrium data so obtained for the binaries *m*-cresol–*p*-cresol, *m*-cresol–acetic, and *p*-cresol–acetic acid are plotted in Figs. 5 and 6.

Determination of binary eutectic curves

To locate the binary crystallization curves in the ternary system, *m*-cresol–*p*-cresol–acetic acid, the disappearance or appearance points were determined for a large number of synthetic mixtures over the entire concentration range using the same apparatus as described above. Ternary mixtures investigated were usually prepared by adding an accurately weighed quantity of the pure component into a mixture of the other two components of known composition, and thus covering the mixture compositions lying in a vertical section passing through one of the corners of the temperature composition prism. Starting with different binary mixtures, the whole concentration range was thus investigated. The disappearance points of the ternary mixtures lying in any one vertical section were plotted against their respective compositions, expressed on the basis of the percentage amount of the third component in the original binary mixture. The minimum point or points in these curves represent the points on the binary crystallization curve or curves which are cut across by the vertical sections.

These minimum points when plotted on an equilateral concentration triangle (Fig. 7) trace out the binary crystallization curves. These curves tend to converge into the two points representing the compositions of the two ternary eutectic points. By working with mixtures near the possible intersection point of the binary eutectic curves the eutectic ternary composition was determined. The composition so determined was verified by noting whether it froze or melted at a constant temperature like a pure component.

Separation of the two phases in equilibrium

The apparatus used for separating the two equilibrium phases is indicated in Fig. 4. It consisted of a jacketted equilibrium tube *E* (about 1¼ in. in diameter) in the top part of which was fused a quickfit socket joint in which fitted a brass cone carrying a stirrer assembly. The lower part of the tube carried a sinter glass plate within it and a bottom connection through which the liquid phase was withdrawn. The desired temperature in the equilibrium tube was maintained by circulating cold alcohol through the jacket round it. The cooling and the temperature control systems were arranged as shown in the figure. The seepage of the liquid through the sinter disc while it was being maintained at the equilibrium temperature was prevented by filling the free volume below the disc with mercury, the level of which could be raised or lowered with the help of the mercury reservoir *W* as shown. When the equilibrium conditions were reached, the mercury was withdrawn through the side arm and the mixture was filtered to the receivers placed below by applying vacuum to them. First the liquid phase was withdrawn and collected in one of the receivers *B*. The crystals remaining behind (together with the entrained liquid) was then allowed to melt by stopping the alcohol circulation and was thereafter withdrawn into the other receiver.

This apparatus was found to be very satisfactory from the points of view of quick filtration, ease of operation, and minimum transfer losses. The filtration was normally over within a fraction of a minute except when the solid to liquid ratio was high and the liquid phase very viscous, these conditions being usually encountered at temperatures lower than − 15°C. Even for such cases, the filtration time was never higher than 2-3 min.

In some of the runs, attempts were also made to remove as much as possible of the entrained mother-liquor from the crystals by displacement washing. Most of the common organic solvents were found miscible with the cresols and hence the sodium chloride brine saturated at the equilibrium temperature was employed for washing. This was, however, not tried for all the runs as it introduced fresh complications such as the preferential washing of acetic acid by the brine and an increase in the time cycle of filtration, especially at the low temperatures.

Analysis of binary and ternary mixtures

For the estimation of acetic acid, an accurately weighed amount of the ternary mixture (about 1 g) was diluted to 100 ml. An aliquot of 25 ml was then titrated with N/10 sodium hydroxide, using as an indicator a mixture of equal amounts of 0·1% solutions of bromthymol blue and cresol red, which gave a sharp colour change from yellow

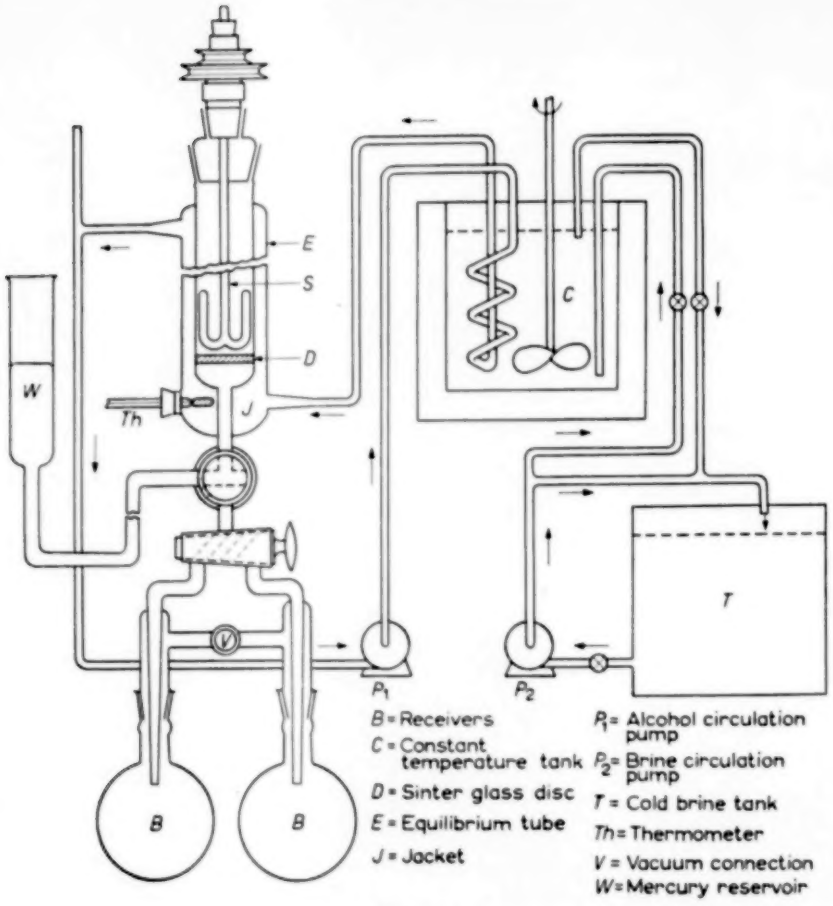

Fig. 4.

to dark green at *p*H 7·5. The method was found capable of giving results accurate to within ± 0·1%.

For the estimation of cresols, about 25 ml of the same ternary mixture were distilled in a fractional distillation assembly until the residue in the still as tested was completely free of acetic acid. The fraction coming over thereafter contained cresols, and although some cresols were lost during the removal of acetic acid, it was found that their relative proportions remained unchanged. This is because the vapour pressures of these two cresols and their mixtures are found to be identical over the entire concentration range [12]. Presence of acetic acid also is found to be ineffective in preferentially lowering the partial vapour pressure of any one cresol in the mixtures [18]. Disappearance points of the acetic-acid-free mixture were then determined with the apparatus previously described, and its composition was read from the binary temperature-composition diagram as determined. The accuracy of this method, checked with synthetic mixtures, was found to be within 2%.

Discussion and Results

A. *Binary solid-liquid equilibrium diagrams*

These diagrams for the three binary systems are represented in Figs. 5 and 6. Both *m*-cresol–acetic acid and *p*-cresol–acetic acid are single eutectic systems, while the binary *m*-cresol–*p*-cresol is a two-eutectic system, accompanied with a compound formation. It may be observed that the phase behaviour of both the cresols with acetic acid is very similar, particularly in the acetic acid rich region wherein the freezing temperatures of various binary mixtures are almost identical and determined by the amount of cresol (irrespective of which one) in the original mixture. The *m*-cresol–*p*-cresol system has been studied previously by Dawson and Mountford [6] and

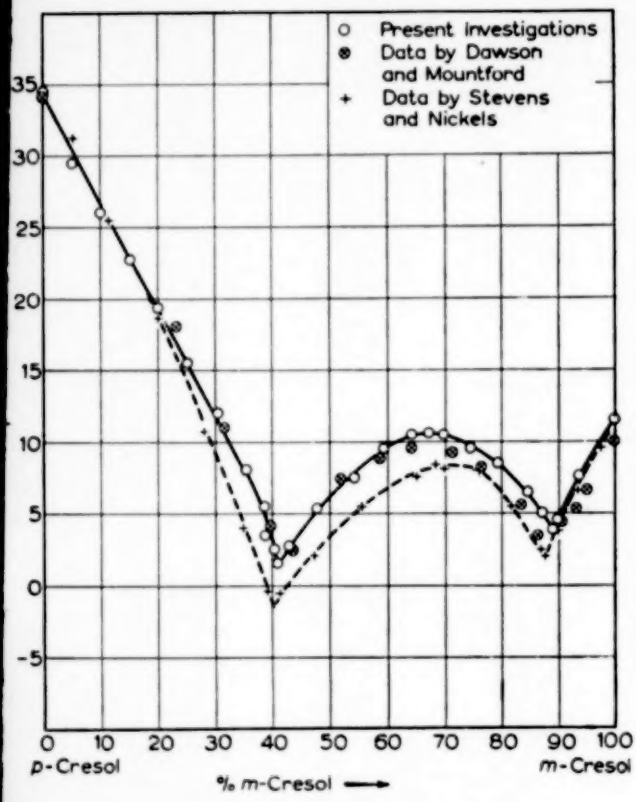

FIG. 5. System *m*-cresol–*p*-cresol.

also by STEVENS and NICKELS [20] whose is a more recent work. The melting points of the cresols used by us and of the cresols used by the latter were almost identical and, in spite of this, a fair divergence is observed in their and our results. This divergence can therefore be explained only on the basis of the method employed for the determination of freezing points. In view of the difficulty of supercooling with cresol mixtures, in the present work only the disappearance points were determined with about 25 g of the sample which was kept mechanically stirred. As against this, STEVENS and NICKELS used 5-10 g of the sample, employed seeding and hand-stirring with a wire loop, and considered the maximum temperature reached during freezing as the correct temperature. Such a procedure for a mixture and one which supercools considerably even when seeded was not found satisfactory by us, and hence only the disappearance points which were found to be always reproducible were relied on. The method of thermal analysis also was not found satisfactory in view of the difficulty of supercooling of the cresols.

The melting points of the pure components employed and the eutectic data as determined, are presented in Table 1 given below.

B. *The ternary system*

The concentration triangle for the ternary system as determined is represented in Fig. 7. In this diagram R and S are the two ternary eutectics, while the curves $N'R$, $K'R$, $F'S$ and $J'S$ are the four binary eutectic crystallization curves. QR and QS can also be considered as pseudo-binary crystallization curves. These curves were located by plotting the composition of the minimum point or points obtained in the primary crystallization curves for various vertical sections judiciously chosen to cover the entire concentration range. Along the curves $N'R$ and $F'S$,

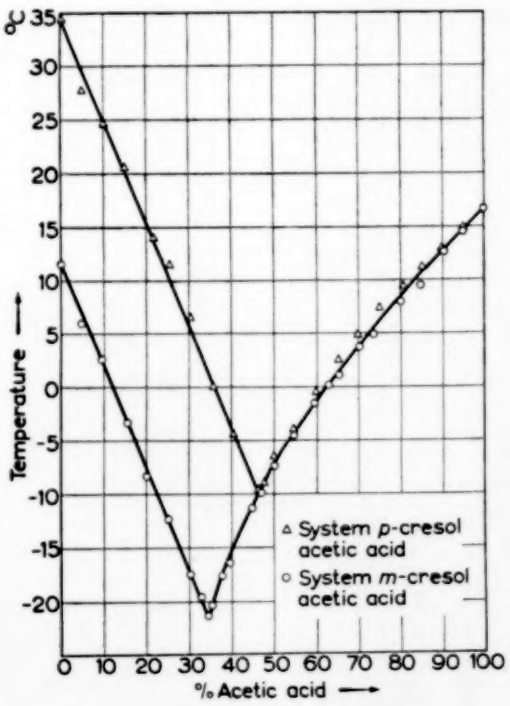

FIG. 6.

acetic acid with either *p*-cresol or *m*-cresol will co-precipitate, while along the curves *K'R* and *J'S* binary compound *V'* with either *p*-cresol or *m*-cresol will crystallize out. Similarly, along the pseudo-binary crystallization curves *QR* and *QS* acetic acid will co-precipitate with the compound *V'*. Thus, if the purpose is to separate the two cresols, the concentration region *CRSBC* should be avoided. The composition of *m*-cresol in the commercial mixtures is usually of the order of 60%, which lies between the composition (on the acetic-acid-free basis) of the two ternary eutectics, and therefore it is evident that just adding acetic acid alone to it and crystallizing will not effect the separation of the two cresols. This will be possible only when the ternary system with the solvent is a peritectic type in which both the true eutectic and the peritectic points lie on either left or right of the line *AP* where the point *P* represents the composition of the commercial mixture. Also the percentage amount of either of the two cresols which can be recovered in the pure form from the mixture *P* will depend upon the distance of the nearest eutectic point from the line *AP*. The greater this distance, the greater will be the temperature and consequently the concentration range over which the separation can take place. Similarly, it is obvious that the separation of one of the components in the pure

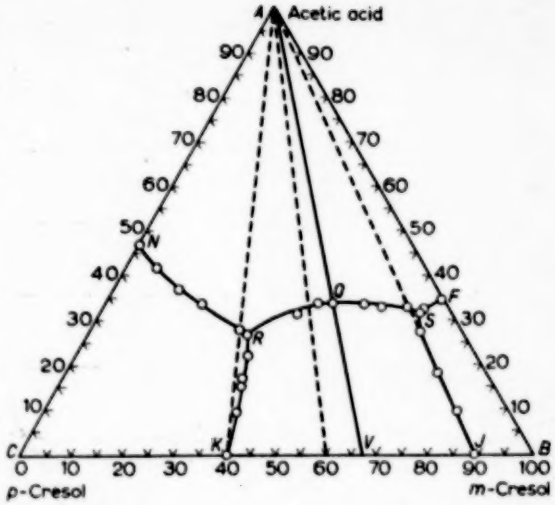

Fig. 7. System *m*-cresol–*p*-cresol–acetic acid.

form from a binary eutectic will take place only if the composition of the ternary eutectic (expressd on the solvent-free basis) is different from the composition of the original binary eutectic mixture ; and the larger will be such a separation, the greater the difference in the ratio of the amounts of feed component in the binary and the ternary eutectic mixtures. As will be seen from the concentration triangle, the two ternary eutectics in this case do not lie very far away

Table 1.

		Present investigation	Dawson and Mountford [6]	Stevens and Nickels [20]
p-cresol	Melting point, °C	34·5	34·15	34·7
First Eutectic	Composition, % *m*-cresol	40·5	43·0	40·0
	Melting point, °C	1·5	1·2	− 1·0
Binary compound	Composition, % *m*-cresol	67·0	66·7	70·0
	Melting point, °C	10·6	9·7	8·4
Second Eutectic	Composition, % *m*-cresol	89·0	88·0	88·0
	Melting point, °C.	3·8	2·0	2·0
m-cresol	Melting point, °C	11·5	11·0	11·5

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Table 2.

Series No.	Temperature of equilibrium, °C	Composition of the feed, %			Composition of the melt, %						Composition of the residue after filtration (solid phase and entrainment), as observed			Region of Crystallisation	Recovery of the desired component in crystals (calculated), %		
					m-cresol		*p*-cresol		acetic acid								
		m-cresol	*p*-cresol	acetic acid	Calculated	Observed	Calculated	Observed	Calculated	Observed	*m*-cresol	*p*-cresol	acetic acid		Basis composition of melt as observed	Basis composition of melt as calculated	
1a		10·0	69·5	20·5	11·5	9·8	65·7	66·9	22·8	23·3	5·5	85·8	8·7	Primary	12·2 (*P*)	16·65 (*P*)	
1b	+ 1·5	10·0	69·6	20·4	11·5	11·0	65·7	67·0	22·8	22·0	1·7 (washed sample)	95·4	2·9	Primary	12·2 (*P*)	16·65 (*P*)	
2		18·0	71·9	10·1	23·0	21·9	64·0	65·7	13·0	12·4	5·7 (washed sample)	90·0	4·3	Primary	25·6 (*P*)	31·0 (*P*)	*P* = *p*-cresol *M* = *m*-cresol *A* = acetic acid *V* = binary compound 67% *m*-cresol, 33% *p*-cresol
3		26·2	65·8	8·0	32·2	32·2	57·3	58·3	10·5	9·5	13·4	81·6	5·0	Primary	29·6 (*P*)	30·5 (*P*)	
4	− 1·5	16·0	65·6	18·4	17·5	17·3	61·0	61·3	21·5	21·4	4·9 (washed sample)	92·1	3·0	Primary	21·0 (*P*)	20·5 (*P*)	
5		10·5	14·8	74·7	16·8	16·0	24·2	23·4	59·0	60·6	–	–	85·0	Primary	47·2 (*A*)	49·0 (*A*)	
6		22·9	3·1	74·0	36·0	35·0	4·5	5·5	59·5	59·5	–	–	88·2	Primary	48·6 (*A*)	49·5 (*A*)	
7		86·5	4·5	9·0	84·5	83·8	5·5	5·7	10·0	10·5	91·0	3·4	5·6	Primary	23·2 (*M*)	16·8 (*M*)	
8	− 18·0	43·3	28·5	28·2	40·5	40·4	28·0	27·9	31·5	31·7	48·6	27·2	24·2	Primary	18·5 (*V*)	17·5 (*V*)	
9	− 18·5	5·1	44·3	50·5	16·0	18·0	49·0	48·5	35·0	33·5	4·1	44·4	51·5	Binary	68·5 (*P*)	65·6 (*P*)	
10		10·8	55·3	33·9	16·0	18·0	49·0	48·5	35·0	33·5	7·3	58·7	34·0	Binary	42·5 (*P*)	46·7 (*P*)	

from the lines $K'A$ and $J'A$, and as such not much separation of the two binary eutectics (K' and J') in the presence of acetic acid is to be expected. Attempts were made to resolve the above two eutectic mixtures for the two cresols, but the separation theoretically expected being very low and the experimental errors involved being comparatively large, no conclusive results were obtained.

However, a large number of runs were carried out on the separation of mixtures lying outside these eutectic compositions, and some of the results obtained are recorded in Table 2. On the basis of the equilibrium temperature-concentration triangle as determined, and the lever rule, the per cent recovery expected from each run at any given temperature has been calculated, and these figures are also included in the same table for comparison. To explain the procedure followed in calculating the per cent recovery of one of the components in its pure form at any given temperature of crystallization, consider the mixture of the composition 16% *m*-cresol, 65·6% *p*-cresol and 18·4% acetic acid (Run No. 4, Table 2) maintained at an equilibrium temperature of − 1·5°C. By interpolation, it is found from the disappearance point data of mixtures that the composition of the liquid in equilibrium with the solid at − 1·5°C should be 17·5% *m*-cresol, 61·0% *p*-cresol, and 21·5% acetic acid. The composition of the equilibrium liquid phase as collected analysed 17·3% *m*-cresol, 61·5% p-cresol, and 21·4% acetic acid, indicating fairly good agreement between the calculated and the observed values, particularly in view of the fact that the composition of the equilibrium liquid phase was arrived at by interpolation of the disappearance-point data on mixtures. These data for various runs carried out are included in column 3 of Table 2. In column No. 4 are given the compositions of the residue (as recovered after filtration) consisting of the solid phase and the entrained liquid. If it is assumed that the liquid entrained has the same composition as that of the equilibrium liquid phase, the composition of the solid phase as recovered will be obtained by drawing a straight line through the points representing the compositions respectively of the residue, the equilibrium liquid, and the feed mixture. Following this procedure, the composition of the solid obtained is indicated in Fig. 8, and the line drawn through the points representing the compositions of the feed mixture and the equilibrium liquid (as calculated) illustrates the divergence between the two results, and it will be found that it is well within the experimental error. On the basis of the compositions of the solid phase arrived at as above, the percentage amounts of the desired component, calculated on the basis of its amount in

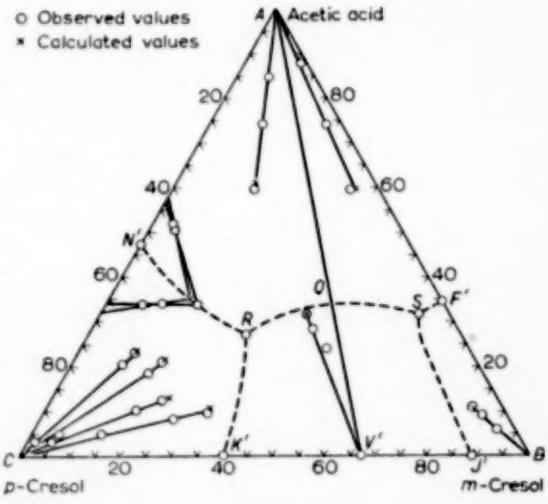

Fig. 8.

the feed mixture, are also calculated, and are represented in column 6 of the same table. These figures for the mixture taken for example are 21·0 and 20·5 respectively. Divergence in some other cases is rather high and is mostly to be attributed to the error involved in the estimation of the correct composition of the equilibrium liquid, and to a smaller extent to the inaccuracy involved in the analysis.

Conclusion

The solvent employed – acetic acid – to separate *m*-cresol and *p*-cresol from their mixtures by extractive crystallization, is not particularly suitable, as the composition of the two ternary eutectics on the solvent-free basis are not

very different from those of the corresponding binary eutectics between the two cresols. This work, however, does conclusively prove that the extractive crystallization process is a potential method of separation if a suitable solvent is found.

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Book reviews

High speed aerodynamics and jet propulsion, Vol. I. Thermodynamics and Physics of Matter. F. D. Rossini (Editor). Oxford University Press, 1956. p. 812 + xviii. 100s. (in U.K.).

This work, to be completed in twelve volumes (of which the first is here reviewed), is intended to " bring together, in convenient, highly accurate, and well organized form the basic information that has evolved in the last decade in the related fields of gas dynamics, aerodynamics, combustion and jet propulsion." This first volume in the series, edited by Rossini, brings together " the basic principles of thermodynamics and physics of matter, presented from the standpoint of their applicability to a better understanding of high speed aerodynamics and jet propulsion."

Section A, by Rossini, covers the fundamentals of thermodynamics. In section B, Herzfeld and Griffing discuss quantum mechanics, including molecular structure, bond energies, and activation energies; while Hirschfelder, Curtiss, Bird and Spotz discuss statistical mechanics and the kinetic theory of gases. Section C, by Beattie, gives a complete treatment of the thermodynamic properties of real gases and their mixtures. In section D, Hirschfelder, Curtiss, Bird, and Spotz discuss the transport properties of gases. In section E, Rice covers critical phenomena. Section F, by Richardson and Brinkley, presents the theories of liquids and liquid solutions. In section G, Ewald discusses solids and solid solutions. Section H, by Herzfeld, covers relaxation phenomena in gases. In section I, Estermann presents a discussion of gases at low pressures, including molecular beams. In section J, Curtiss discusses the thermodynamics of irreversible processes.

The task of presenting such a wide range of subjects in so short a compass is no easy one, but the reviewer is not convinced that the method used here, of compiling contributions from acknowledged leaders in their fields, is the best, or indeed a good, solution. The defects are those that derive from the method of presentation: there is unevenness of treatment, and there is repetition. Both may be illustrated by comparing the treatments of wave mechanics in sections B and G. There are sections that are simply condensed or rewritten from parts of other books, and it is not always clear what has been gained in the condensation. There is a lack of unity which is perhaps inevitable.

To comment on sections in detail is probably to reflect principally the reviewer's interests. Section A is an adequate introduction, although the ideas of temperature and of scales of temperature have been better expounded elsewhere. Perhaps the most valuable section will be found to be that (section C) on the thermodynamic properties of real gases, where Beattie collects a large number of equations for the evaluation of actual properties in real cases. It may prove to be unfortunate that Rice, in his otherwise excellent discussion of critical phenomena, has done so on the basis of the assumption of a critical region, an assumption that is novel and is still debated. The article on relaxation phenomena in gases is succinct and well documented. That on the thermodynamics of irreversible processes (written in 1951) is now out of date, and fails to point out the potential importance of this field.

A feature of the book is the lists of references and bibliographies to each section, although the reviewer considers that more attempt should have been made to bring these up to date. There are notable absences, for example in the field of thermodynamics, which reflect the long interval between the writing of the section and the date of publication. A defect is the absence of reference tables showing the symbols used and their meanings; this detracts from the usefulness of the book as the work of reference it is intended to be.

The standard of production is high, and so is the price.

H. P. Hutchison

Mass-Transfer Operations. Robert E. Treybal. McGraw-Hill Book Company, 1955. ix + 666 pp. $9.50 (£3 11s. 6d.)

The author has written an integrated account of the chemical engineering applications of mass transfer, and the work is so arranged that the essential similarities between processes involving the same fundamental mechanisms are stressed. The particular features of the book which commend it are the chapters dealing with diffusion in solids and with adsorption. The last-mentioned which also treats ion exchange as a special application of adsorption, gives a useful introduction to a subject which is not included in most general textbooks. The title of the book is, however, rather misleading, since this is not an advanced book on mass transfer. Apart from the items mentioned above, no material is included which one would not expect to find in a reasonably advanced textbook of chemical engineering, and some of the operations are not considered in quite the detail which might have been expected in a book specializing in mass-transfer operations. Thus, only passing reference is made to the penetration theory of Higbie, and nowhere is a method of solution given for the unsteady mass-transfer equation. Air humidification is quite well covered, though the method of calculation of the condition of the gas phase is not given. In the absorption chapter, no reference is made to

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simultaneous absorption and chemical reaction, and the newer centrifugal absorbers are not mentioned. Again, multicomponent distillation is not treated, and the book therefore falls short of the requirements of the honours undergraduate student in this respect. Liquid-liquid extraction is covered very fully, as one might expect in view of the author's interest in the subject, and the chapter on drying is comprehensive, though one would have liked to see a little more on the mechanism of moisture movement in the capillary spaces. The descriptive section of the chapter on leaching is good, but a little more could profitably have been said on the methods of calculation for systems involving countercurrent washing. One of the most useful features of the book is the large number of worked examples, and the inclusion of a wide selection of problems at the end of each chapter for the student to work through himself. Altogether, the book is a well-written exposition of the subject and gives a somewhat novel approach to several of the operations discussed. Except in the field of adsorption, however, it cannot be said to add a great deal to the scope of existing textbooks.

M.W.P.

Journal of the Imperial College Chemical Engineering Society, Volume 8. Love and Malcomson, Ltd., Redhill, 1954. 112 pp. 12s. 6d.

In the eighth volume of the journal, the high standards set by the preceding volumes have been maintained. This publication is not simply a house journal of the Imperial College, but contains a number of original contributions of considerable scientific importance by past and present members of the chemical engineering department. In some cases the work referred to is still in progress, and the journal thus serves to give advance information on subjects to be reported more fully at a later date. Among the subjects included are freeze drying, rheology, measurement of gas solubility at high pressures, and silicones.

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Announcement

Victoria, Australia, offer £1,000 Fellowship in Chemical Engineering

THE Fellowship worth £1,000 (Australian) is offered in Chemical Engineering by the British Memorial Fund, established in Victoria, Australia, by public subscription. The Fellowship is a gesture of "loyalty, gratitude and affection" to the British people in recognition of their "rôle in saving civilization in the Second World War."

It provides for ten months' study in Victoria for the selected candidate and covers travelling and living expenses during the period.

Accommodation will be arranged by the Fund. Wives and children are welcome but no extra expenses can be paid to cover them. The upper age limit for both men and women is 35 years, and applicants must be of British stock of at least ten years' residence in the United Kingdom.

The Fellowship is open to workers in any aspect of chemical-engineering research or chemical-engineering education who could benefit by their participation in the development of this science in Australia. The following topics are listed as a guide to the types of investigation work which might be undertaken by the Research Fellow :

1. Economic and production problems of chemical manufacture in Australia.
2. Process efficiency – methods of investigation.
3. Gas turbines in chemical industry.
4. Water purification and conservation in arid areas.
5. Chemical engineering in extensive agriculture.
6. Dynamics of road surfaces subject to heavy traffic.
7. Free radical mechanisms in chemical industry.
8. Furnace design and combustion efficiency.
9. Heat and mass transfer to and from the atmosphere.
10. Zone refining with particular reference to solutions of inorganic salts.
11. Dimensional factors in heterogeneous catalytic process.

The necessary arrangements and general direction of research work will be the responsibility of I.C.I. Australia and New Zealand Ltd., who have their headquarters and major research facilities in the State of Victoria.

Simultaneously with the Fellowship in Chemical Engineering, a Fellowship in Natural History and two others where applicants may choose their course of study or research are being offered by the Fund.

Members of the London Selection Committee are :

Col. the Hon. W. W. LEGGATT – *Chairman*
Lady ALBEMARLE — Lord HUNTINGFIELD
Lord BAILLIEU — Sir VINCENT TEWSON
Sir ANGUS GILLAN
Dr. J. F. FOSTER
(*Secretary* – Association of Universities of the British Commonwealth).

Full details can be obtained from Col. the Hon. W. W. LEGGATT, Agent-General for Victoria and Chairman of the British Memorial Fund, London Section Committee, Victoria House, Melbourne Place, Strand, London W.C.2. Closing date for the receipt of applications – 15 September 1956.

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